CHAIN SCISSIONABLE POLYMER BASED PHOTORESIST FOR EUV (EXTREME ULTRAVIOLET) LITHOGRAPHY

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By

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ABSTRACT

Ever since its inception in 1965, Moore's law has served as a guiding beam for the semiconductor industry. Following this rule, researchers have succeeded in doubling the number of transistors biennially. In recent years, next-generation lithography technologies such as extreme ultraviolet lithography (EUVL) have proven to be instrumental in keeping up with this trend. The choice of photoresist for EUVL is a key factor enabling high-resolution patterning (<10 nm) in a single step process. However, in order to achieve such small feature sizes, we need to simultaneously satisfy the resolution, line edge roughness (LER), and sensitivity requirements known as RLS tradeoff. Another major concern with EUVL is the problem of stochastics variation within photoresist due to the photoelectric and molecular reactions during UV exposure. Therefore, a new approach to overcome these challenges is needed and we believe that low ceiling temperature (T_c), chain scissionable, depolymerizing photoresists are a promising option.

This research focuses on the lithographic evaluation of a potential EUV photoresist containing derivatives of polyphthalaldehyde (PPA) combined with photoacid generators (PAG) and base quenchers (BQ). The role of PAG and BQ in improving the LER and resolution of the photoresist was investigated. Several ionic and non-ionic PAGs in combination with PPA were studied to evaluate the sensitivity of the photoresist. The lithography processing conditions such as UV exposure dose, post exposure baking, and non-aqueous development were systematically studied and optimized. This work aims to guide and promote the design of scissionable, depolymerizing photoresists for next-generation EUVL.

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BIOGRAPHICAL SKETCH

Abhaiguru Ravirajan was born in Chennai, India. He earned his B.Tech in Chemical Engineering in 2018 at SSN, Anna University. During his undergraduate studies, Abhai worked on plasmonic resonance using COMSOL Multiphysics under the guidance of Prof. Tiju Thomas. This work earned him his first publication and made him realize his interest in research. Inspired by Prof. Thomas, an alumnus of Cornell, Abhai decided to pursue his MS in Chemical Engineering at Cornell University. His interest in Light-matter interaction steered him towards Prof. Christopher Ober's research group who worked on various projects related to lithography. He was eager to work in the cleanroom where he enjoyed learning new equipment and mastered several nanofabrication techniques and characterization. Outside the cleanroom, he enjoyed volunteering for ASHA Cornell and teaching the Tamil language at the Department of Asian Studies. He plans to join the semiconductor industry and become an integral part of a community that believes in and works tirelessly to keep up with Moore's law.

Dedicated to my parents for their unconditional love and support

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CHAPTER 1

INTRODUCTION

1.1 Background

An integrated circuit (IC) is a micro sized chip, holding millions of transistors, resistors, and capacitors on a semiconductor wafer. A variety of physical and chemical modifications are performed on this semiconductor substrate to make an IC. These modifications generally fall following categories: film deposition, patterning, into the and semiconductor doping. A modern micro-electronic device is a complex circuit built by integrating millions of transistors created by these processes. The root to all these processes is lithography, i.e., the formation of three-dimensional relief images on the substrate for subsequent transfer of the pattern to the substrate. In 1965, Gordon Moore described the progress of integrated circuits in a prediction known as Moore's law. Based on Moore's law, the number of transistors per square inch of an integrated chip would be double every two years¹. If Moore's law is applied to other industries; for example, the Apollo space program that landed humans on the moon in 1969 cost \$25 billion and took three days. If prices for space travel fell at the pace of Moore's Law, today that program would cost the same as a private jet and the trip would now take one minute. Figure 1.1 shows the transistor count trend following Moore's law.

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*Figure 1.1. Transistor count trend for microprocessors*²*.*

The patterning of integrated circuits on Si wafer is established by a photographic process referred as optical lithography in which a light sensitive material known as photoresists is irradiated by Ultraviolet (UV) source and developed to form three-dimensional relief images on the Si substrate. The steps of this critical manufacturing process are listed in Figure 1.2.



Figure 1.2. Various steps in the lithography process.

Wafer pretreatment is a substrate preparation technique to remove contaminants and improve the adhesion of the photoresist material to the substrate. Substrate contamination can in the form of organic or inorganic particulates and are generally removed by chemical, ozone, or plasma stripping. In order to enhance the adhesion, sometimes it is adhesion promoters like HMDS necessary to deposit (hexamethyldisilazane) that replace the -OH group with an organic functional group that offers good adhesion to photoresist. A thin, uniform coating of photoresist at a controlled thickness is achieved by spin coating. In this method, photoresist is dispensed in liquid form onto the wafer which is then spun about its axis. The density of the resulting photoresist film is often insufficient to support further processing. Softbake or prebake is used to remove the residual solvent and densify the resist film. Upon exposure to light photoresist undergo photochemical reactions in the targeted areas through the mask and the objective lens system. Post exposure baking is used to drive additional chemical reactions or the diffusion of components within the resist film. Finally, the exposed wafer is introduced to a developer to selectively remove the photoresist. At this stage either the exposed or unexposed areas of the polymer film gets dissolved in the developer and produces positive or negative tone images, respectively.

1.1.1 Introduction to lithography

The importance of lithography can be understood in two ways. Lithography accounts for about 30% of the total cost of Integrated circuit manufacturing due to the complexity and large number of steps of steps involved. Second, lithography tends to be the technical limiter for further advances in feature size reduction and thus transistor speed and silicon area³⁻⁴.

According to Rayleigh's Resolution equation,

$$R = k1 \times \frac{\lambda}{NA} \tag{1}$$

and Rayleigh's Depth of Focus equation,

$$DOF = k2 \times \frac{\lambda}{NA^2} \tag{2}$$

the resolution(R) and depth of focus (DOF) is related by the numerical aperture (NA) and wavelength (λ) of light used for pattering the photoresists, where the terms k1 and k2 are constants and can be modified by the lithographic materials and the exposure tools⁵.

From Rayleigh's law we understand that smaller the wavelength of light, smaller the linewidth that can be imaged, which motivates the manufacturers to utilize the photolithographic tool smallest wavelengths possible. In the 1980's improvements were first made by decreasing the exposure wavelength λ from the 436-nm (mercury gline) wavelength to the 365-nm (i-line) wavelength, and on to 248 nm Deep Ultraviolet (DUV) lithography, which has assisted feature sizes to minimize while maintaining a practical depth-of-focus⁶. With the use of deep ultraviolet excimer lasers (248 nm with KrF laser; 193 nm with ArF laser), the industry saw its first major transition in 1990's. In addition to this, the numerical aperture (NA) of the projection tool was studied, despite knowing that the increase of NA could only be detrimental to the field depth.

In the last twenty years, semiconductor industries have been relying on 193nm immersion lithography. As the name implies, light with a wavelength of 193 nm is used for transferring the pattern on photomask on to the Silicon wafer. With the 193nm wavelength light cannot directly define features smaller than its own wavelength which is much longer than the modern day requirements. Also, 193nm immersion lithography uses pure water as immersion medium which improves the NA value as high as 1.35. Defects in photoresist patterns are produced due to the direct contact of the resist film with the water which allows polar substances in photoresists to be dissolved. The contaminated water can further corrode the lens that comes in contact with it⁷.

Following 193nm lithography, 157nm F_2 lithography was an active area of research⁸. The major drawback of 157nm F_2 lithography was the

degradation of organic photoresist material and additive contamination of the immersion liquid. In addition, design, and processing of the projection optical system continued to cause critical limitations in further exploring this technology.

The next generation electron beam lithographic technique was extensively studied for a long time due to its high resolution and stable performance. The concept of ebeam lithography originates from scanning electron microscopy and works by moving a focused electron beam precisely on the sample stage point by point. This direct write lithography technique is very attractive especially in small volume production because it did not require any time consuming mask preparation and is not limited by the wavelength. However, the disadvantage of this technique is that the exposure is achieved sequentially, pixel after pixel on the surface, and each pixel of the graphic needs to stay for a certain time-period, limiting the productivity for high volume manufacturing. Also, with continuous progress of optical lithography, e-beam can no longer claim its superiority in terms of resolution and alignment precision and thus making it as an auxiliary technology in the microelectronics industry.

Another direct patterning lithography technology that looked promising for nanofabrication was focused ion beam lithography (FIBL). FIBL uses finely focused ions and offers higher resolution than electron beam lithography or photolithography, as the ions used in this technique are far heavier than electrons and photons. Similar to electron beam lithography this involves a mask less serial process, and

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the wafer is exposed pixel by pixel and hence the process was slow and can be considered only over very limited sample areas⁹⁻¹⁰.

Despite the major efforts in the 1980s, X-ray lithography never really took off as an industrial technique. Source weakness (even if synchrotrons are huge experimental systems), the difficulty involved in the fabrication of transparent masks and the lack of reduction optics heavily undermined the future of this technique¹¹.

Another alternative technique involves nanoimprint lithography (NIL) which offers high throughput and high resolution. Unlike optical lithographic approaches, NIL relies on direct mechanical deformation of the photoresist through a reusable stamp without modifying the chemical properties of the resists and thus can fabricate features much smaller than the wavelength of light with high precision¹². NIL-based approaches do not have the demanding requirements of semiconductor IC manufacturing, especially in terms of defect control and production-level throughput. However high temperatures and pressures required for the nanoimprinting limits the scope and application of NIL technique¹³.

In order to meet the current industry requirements and to print smaller feature size in fewer steps, Extreme Ultraviolet lithography (EUVL) is considered as suitable technique for sub-10-nm manufacturing¹⁴. Unlike other NGLs such as electron or ion-projection lithography, EUVL belongs to the family of optical lithography and many years of industry learning on optical lithography can be directly applied¹⁵.

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Figure 1.3. Schematic of a EUVL system¹².

Originally named as soft X-ray projection lithography, EUVL operates at exposure wavelength of 13.5 nm and aids in improving imaging resolution, processing time and line width roughness $(LWR)^{16}$. Currently, EUVL is projected to use in manufacturing at the 7-nm node or beyond and possess unique features that differ from conventional DUV and 193nm lithography tools in terms of the light source, reflective optics and reflective reticles compared to the DUV excimer laser source, refractive optics and transmitting reticles¹⁷. Since most materials absorb at 13.5nm wavelength and to prevent optical contamination EUV optical systems are enclosed in vacuum environment. However, the major barrier of EUV lithography for high volume manufacturing (HVM) applications is its low source power and low throughput. The strategy to improve the efficiency of EUV lithography is to intensify the EUV source from currently 10 W to roughly 200 W which remains a formidable engineering challenge¹⁸. Figure 1.3 shows a schematic of an CO_2 laser-produced plasma EUV scanner.

1.1.2 Introduction to EUV photoresist

The choice of EUV photoresist is a key factor for adoption of EUVL in HVM. A promising EUV photoresist should satisfy the industrial requirements of resolution (<10 nm) and line-width roughness (LWR < 15%) at high sensitivity of doses as low as 20 mJ cm⁻² or below¹⁹. However there exists a triangular trade-off between resolution, line edge roughness (LER) and sensitivity, known as the RLS tradeoff as shown in figure 1.4^{20} . RLS performance along with stochastic variations are the key issues for development of highly efficient EUV resist materials.



Figure 1.4. EUV resist RLS trade-off relationship.

Chemically amplified resists (CARs) have emerged as the most commercially used class of photoresist in DUV lithography²¹. The chemical amplification concept was first reported by Ito and Willson at IBM research and quickly applied to the manufacture of DRAMs²². These photoresists consists of a polymer with acid sensitive groups (such as tertiary esters), photo-acid generator (PAG), base and solvent They work on the principle of acid generation during light exposures, followed by acid catalyzed reactions which further changes the solubility of the photoresist in developer²³⁻²⁴. For these systems, one molecule of photogenerated acid can lead to string of subsequent reactions, thus the name chemically amplified. CARs were widely accepted in industries due to their superior properties such as enhanced sensitivity, high contrast and high resolution²⁵. According to the imaging mechanisms, the chemically amplified resists can be classified as following systems; deprotection, depolymerization, rearrangement, intramolecular dehydration, condensation, cationic polymerization. Many research groups have extensively studied the deprotection and condensation systems for the design of aqueous-basedevelopable positive and negative resists²⁶⁻²⁷. Figure 1.5 displays a specific example of acid-catalyzed deprotection chemistry (tBOC Resist)^{21, 28}.



Figure 1.5. Acid-Catalyzed Deprotection Chemistry (tBOC Resist)²¹.

Three-component negative system consisting of a novolac resin, a photochemical acid generator, and a melamine cross-linker was the first commercial chemical amplification resist was which undergoes acid-catalyzed condensation with the phenolic resin²⁹. Figure 1.6 shows the cross-linking of a novolac resin through acid-catalyzed condensation with a melamine for negative aqueous-base development³⁰.

In case of CAR, diffusions of photo acids remains to be a problem of LER³¹. International Roadmap for Devices and Systems (IRDSs) requires 1.2 nm metal LWR for the 5-nm node but are yet to be achieved³². The uncertainty in the development of CARs as EUV photoresist and whether they would be able to satisfy the LER requirements for future lithography nodes has led to the investigation of non-traditional resists, such as chain scissionable resists³³, polymer bound PAG resists³¹, branched polymer³⁴, inorganic resists³⁵, molecular glasses³⁶, and non-chemically amplified resists (non-CARs)³⁷⁻³⁸.



Figure 1.6. Acid-Catalyzed condensation reaction of aminoplast cross linker with novolac resin³⁰.

The Whittaker's group and Blakey's group from University of Queensland employed multiple polycarbonate based non-Chemically amplified EUV resists as EUV photoresists³⁹. In contrast with CARs, non-CARs formulations usually only consist of two components, the polymer and solvent. Positive-tone non-CARs absorb photons and secondary electrons, which induces polymer backbone scissions and fragment into low molecular weight segments have higher solubility in developer. This design was able to achieve 28.6 nm feature sizes.

In 2004, a group of researchers proposed a new concept for photoresist materials, molecular resists⁴⁰. These amorphous molecular materials possess resist properties which have advantage over polymer materials due to their smaller molecular size. Molecular Glasses (MGs) have the ability to combine the benefits of polymers such as an amorphous structure, thermal stability and thin-film forming ability with the characteristics of small molecules, such as high purity and a well-defined structure. Shirota and co-workers from Osaka University successfully reported an electron beam molecular glass resist system based on disk-like tri(hydroxyphenyl) molecules whose T_g 's were relatively low around 70 °C ⁴⁰. Ober group further extended this work by designing a larger molecule with six phenolic groups, attached to the central benzene moiety, with hydroxyl substituents in alternating meta and para positions³⁶.

Henderson and coworkers designed A series of single-component molecular resists with PAGs covalently bonded to the MG core. The primary benefit of single component multifunctional system is the ability to produce truly monodisperse resists that can be spin coated to form homogeneous films, since there are no physical blending of additives such as PAGs or base quenchers. They provide the platform to include high PAG loadings in the resists which will increase the sensitivity and improve the LER. This design approach helps in having a very uniform acid diffusion coefficient throughout the film and provides the ability to precisely control the photoacid diffusion behavior. Figure 1.7 schematically demonstrates a single molecule CAR. The non-ionic PAG bound MG containing molecular glass core that uses a norbornene dicarboximide PAG (NBB) was able to produce images with a low LER of 3.9 nm and a resolution of 40 nm using ebeam lithography⁴¹⁻⁴². The ionic single molecular resists is based on a tBoc protected triarylsulfonium (TAS) core produced patterns with resolution of 55nm and a low LER (3σ) of 3.9 nm with high resolution 100 keV e-beam lithography. Figure 1.8 shows the structures of single component molecular resist. The non-ionic resist showed multiple improvements compared to the ionic system including reduced dark loss, improved resolution, and solubility. Both resists successfully demonstrate the feasibility of using a single component molecular resist system with high PAG loading.



Figure 1.7. Schematic of the single-molecule multi-functional CAR $design \ concept^{41}$.



Figure 1.8. Structures of the single-component molecular resists TAS - tBoc protected triarylsulfonium (TAS) core NBB - non-ionic norbornene dicarboximide PAG based system (NBB).

In 2002, Ober group has developed several types of organoelement resists using only low absorbing elements, including H, C, Si and B. By using hydrosilylation chemistry or selecting silicon-containing monomers they have made several types of block and random silicon-containing resists⁴³. In 2015, Inpria Corp. introduced the first and second generation metal oxide based resist systems involving hafnium and tin as the primary metal⁴⁴⁻⁴⁵. Tin based metal oxide photoresist produced 13 nm lines and space patterns with the sensitivity of 35 mJ cm⁻². Recently, researchers from Ober group have extensively worked on hafnium and zirconium oxide nanoparticles and continued to focus on developing zinc organic cluster resist with controlled molecular weight and size distribution⁴⁶⁻⁴⁷. The single molecule size, extremely small Zn-based clusters fabricated nanostructures <15 nm in width using EUV lithography.

In 2017, Montgomery et al. from Irresistible Materials (IM) developed a new EUV resist system based on the concept of multi trigger system. Similar to CAR, the resist exposure in multi trigger materials proceed via catalytic process, however in this resist system multiple initiators trigger multiple acid sensitive molecules which then react with each other to cause a single resist event while also regenerating the photoinitiators⁴⁸. This new approach eliminates the requirement of PEB leading to lower cost of ownership by saving process time need for PEB and demonstrated high sensitivity and resolution. Figure 1.9 shows the schematic mechanism of multi-trigger approach. Based on the reports from IM, this system has delivered 25 nm patterns at an exposure dose of 11.4 mJ/cm².



Figure 1.9. Mechanism of traditional chemically amplification and multi-trigger approach⁴⁸.

1.1.3 Introduction to chain scissionable photoresist

Among the emerging platforms of EUV photoresists, PAG tethered CAR, metal-organic hybrid nanoparticles and irresistible materials have shown good performance benchmarks. As EUVL approaches high volume manufacturing, an important area of concern to solve is LER caused by stochastic noise⁴⁹. At present the discussed photoresists alone do not solve the issue of stochastics. The stochastics noise in EUVL arises due to availability of fewer photons per unit dose and only a fraction of these photons are absorbed by the photoresists. Also, as we progress to fabricate smaller features, there is so less area to collect the EUV photons⁵⁰. Increasing the exposure dosage to limit stochastics noise is a solution however it adversely affects the throughout and cost of fabrication. Several approaches to EUV photoresists are being actively pursued and we believe scissionable photoresist designed to depolymerize when exposed to radiation are excellent candidates to tackle low photon stochastics.

Scissionable polymers can be largely classified into – a) main chain scissionable polymers and b) sidechain scissionable polymers. The sidechain scissionable polymer type is the most successfully used type applied to DUV lithography. The solubility contrast based on the change in polarity occurs due to side-chain replacement in this kind of polymer type. But, the disadvantage of side-chain scission type is the formation of large polymer agglomerates resulting in large LWR. One such system involving side-chain scissionable polymers was developed in the 1980s by Fretchet and coworkers who conducted pioneering work in the field of chemically amplified resist systems⁵¹. They made use of the well-documented thermal cleavage of tert-butyl esters and carbonates where the thermolysis temperature was brought down to below 100 °C. The "t-BOC resist" which contains a mixture of poly[4-[(tert-butyloxy-carbonyl)oxy]styrene] (PBOCST), a polymer with labile tert-butyl carbonate side groups and triphenylsulfonium hexafluoroantimonate, a photoactive compound that generates a strong acid. This photoresist liberates strong acid upon irradiation to light. The mechanism of operation of this resist is shown in Figure 1.10 Exposure of the resist creates a latent image of exposed areas with strong acid dispersed in the tert-butyl carbonate-containing polymer along with the unchanged unexposed areas. When heated to 100 °C the acid catalyzes the decomposition of the t-BOC with release of CO₂ and isobutylene. This reduces the thickness of the resist film in the exposed areas. Owing to the low temperature, the unexposed areas remain unaffected. The chemical composition of the exposed region is phenolic while the unexposed regions is carbonate.



Figure 1.10. Mechanism of thermally depolymerizable resist system⁵¹.

Polyphthalaldehyde which is a capped polyacetal was used along with a radiation sensitive substance that generates an acid upon irradiation. This creates a self-developing positive resist which operates based on ceiling temperature phenomenon. The basis of this process is that the photogenerated acid on the exposed areas of the polymer catalyses the thermal reversion of the poly-acetal into monomeric phthalaldehyde. This resulted in an image that appear quite attractive. However, it may be advantageous to incorporate a certain activation energy to avoid volatile substances that may contaminate the instrument²².

MacDonald et al. worked on alternative designs using multiple main chain scission and studied chemically amplified imaging materials based on polycarbonates, polyether, and polyesters⁵². Their work was based on the idea that the cleavage of tert-butyl carbonates or esters need not be restricted to the polymer side chain alone but also be used in the polymer backbone. In this design, the acid-catalysed cleavage processes occur at the main chain. The photogeneration of the acid within the backbone of the polymer, followed by simple heating results in the scission and a subsequent reduction of molecular weight. Figure 1.11 shows examples of acid-catalyzed imaging systems based on multiple main-chain scission.



Figure 1.11. Acid-catalyzed resist mechanism based on multiple mainchain scission⁵².

In 2003, Eschbaumer et al. incorporated the concept of main-chain scission to reduce the influence of polymer size on the patterns printed. In MCS (Main Chain Scission), the polymers have protection groups within the backbone of the polymer so that the monomer units are formed in the exposed areas after baking. Contrastingly, in common CAR polymers the polarity in the exposed areas change due to exposure, since they have protection groups pendant to the polymer backbone. Both schemes are presented in Figure 1.12a and 1.12b. In common resists, some partly exposed polymer units are present on the pattern sidewall and these have a greater probability to form larger aggregates. Since the MCS do not alter the polarity of the polymeric units, the exposed polymer is reduced to the monomeric size by the

acid that gets generated. Thereby Eschbaumer's group focused on polymers containing acid cleavable tertiary oxycarboxylates. This enabled to synthesize a polymer with high molecular weight polymers with reasonable yields. The line edge roughness when compared to a commercial resist showed 50% lesser LER³³.



Figure 1.12. a) Schematic of a common CAR b) MCS: The protection group within polymer backbone.

Sakamizu and Shiraishi also worked on the reduction of LER based on acid-catalyzed fragmentation of acetal groups on the main chain⁵³. They had previously developed a novolak resin-based CA positive resist (NOR) which suffered from low LER stemming from broad molecular weight distribution (MWD). Hence, they developed an acid breakable resin which has acetal (acid-labile group) in its main chain unlike a conventional CA resist polymer with pendant acid-labile group. The acid catalyses main chain scission and fragmentation to form the former polyphenolic units. Thus, it was concluded that the photoresist (ABR) had a high dissolution contrast that was independent of the MWD and prevent material origin of LER. The surface roughness and LER of ABR was lesser compared to NOR. This acid-catalysed reaction is shown in figure 1.13.



Figure 1.13. Acid catalysed fragmentation of AB resin⁵³.

From the previous section, we understand that reducing the molecular weight of the polymers can reduce the line edge roughness and increase the resolution. But, this reduction in molecular weight is detrimental on the mechanical properties of the resist. Lower molecular weights may lead to photoresist pattern collapse rendering the resist nonfunctional. The minimum possible value of the LER is determined by the size of the polymer. If the size of the polymer segments dissolving are small, then the resolution and LER will not be limited by the size of the polymer chain. The segments are cleaved from the polymer after scission undergo dissolution rather than the entire polymer, the molecular weight is decoupled from LER and resolution. Cao et al. worked on such relatively high molecular weight polymers which may be used to improve properties such as yield stress and Young's modulus. Branching of the polymers can also further improve the mechanical properties. The molecular weight of the polymers may even be way above 10000 g/mol and the branches can have long chains of the size 5000 g/mol or even higher⁵⁴⁻⁵⁵.

In the early 2000s, Felix and Ober described new polymeric materials devoid of fluorinated and silicone containing groups to produce positive tone (sub 100nm) patterns. In addition, acetal-linked photoresist were discussed, whereby acetal-based polymer backbones are more advantageous as the fragmentation of polymer is catalysed by acid formed in water and the acetal bonds have lower activation energy which favors easier cleavage. This allows a highly sensitive and complete chain scission. These acetal-based polymers behaved like positive tone resists in both an aqueous base and supercritical CO_2 ; a remarkable feat since water is polar and the other is non-polar⁵⁶⁻⁵⁷.

Main chain acid labile resists were studied extensively by Ogata et al. They synthesized photoresists for EUV lithography forming acetal linkages via ring opening metathesis polymerization (ROMP) using acetal and norbornene as the monomers. This is expected to give

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extremely low molecular weight resists with monomeric size fractions which are formed due to the exposure to photogenerated acids⁵⁸. It was also possible to incorporate bulky norbornene derivatives into the main chain to form polymers having high glass transition temperature (T_g) . Their method was able to improve LWR and thermal resistance.

Chen et al. studied a resist platform without PAGs where the chain scission occurs due to both molecular weight and solubility switches. This change in polarity is brought by the photolysis of pendant nitrobenzyl esters and scission in the main chain happens through poly (olefin sulfone) backbone, this is inherently sensitive to scission by radiation. Another remarkable feature of poly(olefin sulfone) is that after the irradiation step, they undergo depolymerization when heated which can improve and increase the sensitivity of the photoresist. The prescribed mechanism is explained in Figure 1.14 which shows the formation of biradical in the nitrobenzyl group followed by the chain transfer and eventual deprotection to form a pendent carboxylic acid. The chain scission of the poly (olefin sulfone) occurs by the formation of the radical species, i.e. abstraction of a proton from a carbon on the polymer backbone⁵⁹.



Figure 1.14. Mechanism of main chain scission on poly (olefin sulfone) polymer backbone functionalized with pendant nitrobenzyl esters⁵⁹.

This chapter has summarized the importance of EUV lithography and has reviewed some of the previous efforts in the design of chain scissionable EUV photoresists. The following chapters are organized to demonstrate our efforts at understanding polyphthalaldehyde (PPA) as a low ceiling temperature, chain scissionable, depolymerizing EUV photoresists. the DUV lithographic Chapter 2 discusses evaluation of а multicomponent photoresist containing PPA, photoacid system generators (PAG), and base quenchers. Chapter 3 discusses the EUV lithographic evaluation of PPA and describes an alternative, single component multifunctional photoresist system where the PAG is covalently bound to the main chain of the polymer.

1.2. Motivation

For the next generation of EUVL, a new approach for low exposure doses and sensitive photoresists not affected by low photon stochastics is essential and chain-cleavable photoresists are a particularly promising option. In this work we explore polyphthalaldehyde (PPA) as a potential scissionable resist designed for limited EUV light sources using controlled unzipping of a polymer chain in the area of exposure aided by photoactive compounds. Based on the resist forming capability and lithographic performance, we will continue to investigate PPA as a potential photoresist for EUVL.

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CHAPTER 2

POLYPHTHALALDEHYDE BASED MULTICOMPONENT PHOTORESIST SYSTEM

2.1 Introduction

In recent times, researchers have identified a new strategy for creating reactive solid state materials that involve the conversion of an entire polymer into monomer (or smaller molecular units). Triggering stimuli like mechanical¹⁻², chemical³, thermal⁴⁻⁵, and UV irradiation⁶ have been used to depolymerize an entire polymer chain upon cleavage of an end-cap from the terminus of the polymer⁷.

All polymerization reactions are reversible. The so called ceiling temperature (Tc) is defined as the cross over temperature at which the free energy of the reaction changes from negative to positive⁸. Owing to their inherent thermodynamic instability, low ceiling temperature polymers can be unzipped (depolymerized) completely at room temperature as a response to triggering stimuli⁹.

Polymers such as polyphthalaldehyde (PPA) are known to have a low ceiling temperature, i.e., a temperature at which monomer is the thermodynamically preferred state¹⁰⁻¹⁴. Below Tc, the polymer is the

^{*} The synthesis and characterization of cPPA, Br-*l*PPA and aryl tosylate PAG discussed in this chapter were performed by Jingyuan Deng and Yiren Zhang from the Ober research group, Cornell University.

preferred state. The ceiling temperature of PPA is around -40 °C and is thermally stable up to ~150 °C when it is end capped. Hence, the synthesis of PPA takes place at a temperature well below room temperature and must be end-capped through process like acylation or alkylation to render stability at room temperature¹⁵. Figure 2.1 shows the complete unzipping of PPA by the reaction with specific stimulus like UV irradiations.



Figure 2.1. Head to tail depolymerization reaction of an end-capped PPA in the presence of specific stimuli.

Hector and coworkers have demonstrated the use of cyclic polyphthalaldehyde (cPPA) containing a photo-acid generator (PAG) additive to fabricate photo triggerable transient electronics¹⁶. Gregory and coworkers have extensively studied the use of PPA as self-

immolative polymers (SIPs)¹¹. PPA is also used in various applications such as drug delivery systems, dry developing resists¹⁷, and dry nanolithography¹⁵.

Generally, to design a photoresist the resist components must be soluble in the spinning solvent and must be suitable for the formation of amorphous thin films. In addition to this, it must also have a good adhesion capability to the substrate as well as high transparency at desired wavelengths¹⁸. PPA exhibiting all these characteristics proves to be a promising candidate for EUV lithography¹⁵.

Ito, Willson, and co-workers have reported that PPA containing photoacid generators based on onium salts self-develop to the substrate during exposure to low-dose of UV radiations¹⁵. This self-development is achieved through two stages of chemical amplification: catalytic of acid-labile acetal bonds acidolysis and subsequent depolymerization. However, these self-developing resist materials are impractical in device fabrication as the liberation of volatile species may contaminate the exposure tools. In order to overcome this issue, they established resist systems that do not self-develop during exposure but develop completely by heating after exposure. Figure 2.2 shows 0.25 µm features of self-developed PPA containing diphenyliodonium hexafluoroarsenate as photoacid generator.



Figure 2.2. 0.25 μ m features of self-developed PPA when exposed to 1 μ C/cm² of 20 keV electron beam radiation¹⁵.

Typically, polymer resists are multi-component systems comprising of a polymer resist, photoacid generators (PAGs) and a base quencher¹⁹. Photoacid generators are compounds that undergo photochemical rearrangement when exposed to UV radiation, to generate acid. The exposed PAGs when baked, initiates a chemical reaction, enabling either the exposed/ unexposed regions to be developed²⁰.

The structure of the PAG can significantly influence lithographic performance²¹. The performance of a PAG can be quantified using quantum yield, acid strength(pKa) and size, solubility, miscibility, toxicity, and thermal stability. PAGs can either be ionic or non-ionic. Non-ionic PAGs are typically based on sulfone/sulfonate esters²². Although, certain non-ionic PAGs have showed promising results, ionic sulfone/sulfonate ester PAGs have outperformed non-ionic PAGs in terms of their performance²³. Triphenylsulfonium triflate (TPS

triflate) as an ionic PAG and 4-acetylphenyl p-toluenesulfonate (aryl tosylate) as a nonionic PAG in combination with derivatives of PPA are studied in this chapter as potential EUV photoresist. The structures of PAGs and PPA derivatives discussed in this chapter are shown in Figure 2.3.

Base quencher (BQ) is usually added as another component to the photoresist systems along with PAGs to enhance lithographic performance. Base quenchers act as a proton trap site or a buffer in resists. The primary role of base quencher in a multicomponent system is to reduce acid diffusion outside of the nominally exposed regions. Imaging properties such as line edge roughness (LER), contrast and photospeed are influenced by the addition of base quenchers in resist system^{19, 24-26}. In this chapter we will evaluate the role of base quenchers in the lithographic performance of the resist systems used in combination with PPA and PAGs.



Linear PPA (lPPA)



Cyclic PPA (cPPA)



TPS triflate



Br-Linear PPA (Br-lPPA)



Br-Cyclic PPA (Br-cPPA)



Aryl tosylate

Figure 2.3. Chemical structures of PPA derivatives and PAGs.

2.2 Experimental Section

2.2.1 Materials and Synthesis

All chemicals were purchased from Sigma-Aldrich and VWR and used as received unless otherwise noted. Silicon wafers used for lithographic purposes were purchased from Pure wafer and used as received [Diameter: 100 mm; Type/Dopant: p/Boron; Res: 10 - 20 ohm-cm; Thickness: 500 - 550 µm].

The PPA homopolymers were synthesized by Jingyuan Deng and Yiren Zhang of Ober research group using o-phthalaldehyde and Brphthalaldehyde as the starting monomers.

2.2.2 Characterization

Thermogravimetric analysis was performed using a TA 500 TGA with a heating rate of 10 °C/min under dry nitrogen atmosphere. UV absorbance was recorded by spin-coating the materials onto quartz wafers and measuring absorbance with a Shimadzu-UV3101PC-UV-Vis-NIR photometer. Molecular weights (M_n) and polydispersity (M_w/M_n) of the polyphthalaldehyde samples were determined by gel permeation chromatography (GPC). The GPC was performed on Waters Ambient Temperature GPC equipped with a Waters 410 differential refractive index detector. GPC columns were eluted in 1.0 mL/min with tetrahydrofuran (THF) at 40 °C. Polymer samples were dissolved in THF, concentration 1 mg/mL. Polystyrene standards with narrow molecular weight distribution were used for calibration.

2.2.4 Lithographic procedure

A PPA (5 wt%) and 10-20 wt% PAG (with respect to resist) were dissolved in cyclohexanone. Additionally, 10 mol% tributylamine as base quencher (with respect to PAG) was added to the solution. The solution was stirred for 5 minutes and filtrated using a 0.2 μ m membrane filter and spin cast onto silicon wafer at 3000 rpm for 60 seconds (acceleration 1000 rpm/sec) to form a thin and uniform film. After spin coating, a post apply bake (PAB) was performed at 90 °C for 60 seconds to evaporate the spinning solvent.

The film thickness on silicon wafer was measured using p-10 profilometer and Woollam variable angle spectroscopic ellipsometer at a 70° angle of incidence. Cauchy model was used as the fit function. The thickness of the film was measured before and after the development with non-aqueous solvents.

Patterning of the photoresists were done at the Cornell Nanoscale Facility using ASML 300C DUV Stepper ($\lambda = 248$ nm) and ABM Contact Aligner ($\lambda = 254$ nm). Contrast curves were generated from 1 cm x 1 cm areas exposed to the ASML stepper using 248nm DUV radiations with linearly increasing exposure dosage. Contrast curves at EUV exposure wavelength ($\lambda = 13.5$ nm) were carried out at Intel, Oregon using EUV flood exposure tool. After DUV/EUV exposure, the photoresist films were baked using a hotplate at 60-70° C for 30-60 seconds. Optical microscopy images were captured using the Nikon Digital Sight DS-5M-L1 optical microscope. Atomic force microscopy (AFM) was performed on developed samples with Asylum-MFP3D-Bio-AFM in tapping mode. Further evaluation of exposed patterns were carried out using Zeiss Gemini 500 Scanning Electron Microscope (SEM) and FEI Strata 400 STEM FIB.

The exposed films were developed in non-aqueous solvent yielding positive tone patterns. All the exposed photoresist films were developed in 2-propanol for 120 seconds, blown dry with nitrogen and stored in black fluoroware 100mm wafer carriers.

- 2.3 Results and Discussion
- 2.3.1 cPPA multicomponent photoresist systems
- 2.3.1.1 Solubility and film formation

The solubility and film forming capability of the polymer combined with PAG molecules in common spinning solvents is crucial for further lithographic evaluation and characterization. Cyclic polyphthalaldehyde (cPPA) containing triphenylsulfonium triflate (TPS triflate PAG) and/or 4-acetylphenyl p-toluenesulfonate (aryl tosylate PAG) demonstrated satisfactory solubility in common solvents, such as 1,4 dioxane, diglyme, cyclohexanone. Clear and transparent solutions were obtained even at very high concentrations of solutions of cPPA. The solubility of linear polyphthalaldehyde (*IPPA*) and bromine polyphthalaldehyde (Br-PPA) were as good as cPPA. Figure 2.4a, represents a homogeneous film spin coated from a resist solution of cPPA containing TPS triflate PAG and tributylamine as BQ in cyclohexanone. Further there were no observable impurities when examined by optical microscope as shown in Figure 2.4b.



Figure 2.4. a) PAG and BQ containing cPPA film spin casted on silicon wafer; b) optical microscope image of the cPPA film indicating formation of a defect free homogenous film.

2.3.1.2 Thermal stability

Thermal characteristics of PPA were examined by thermogravimetric analysis (TGA). The decomposition temperature at 5% weight loss of cPPA and Br-*I*PPA was found to be 128 °C and 178 °C, respectively. The higher the decomposition temperature, the more thermally stable the polymer and it is critical in order to determine the optimal pre-bake and post exposure bake temperatures. Also, polymers with good thermal stability exhibit longer resist shelf life.

2.3.1.3 Role of photoacid generators

The conventional photoresists are multicomponent systems containing blend of polymer and PAG as necessary components for а photolithographic process. In order to understand the sensitivity of the polymer itself without the influence of PAG, lithographic evaluation was performed using a 254nm ABM contact aligner on the resist system containing 5 wt% cPPA in cyclohexanone. The resist solution was prepared, spin coated, and PAB applied as described above. The imaging resolution of the ABM contact aligner is about 0.5 µm and hence it is important to note that, high resolution patterning is not the goal of this experiment but rather to understand the importance of PAG. A series of lithography tests were carried out on the pure cPPA photoresist in increasing exposure doses and were post exposure baked (PEB) at 90 °C for 60 seconds. Low contrast images were obtained at very high exposure dosage (2.1 J/cm^2) indicating the poor photosensitivity of the cPPA. Figure 2.6 shows the optical microscope image of a pattern observed when cPPA was exposed to 254nm radiations.



Figure 2.6. Optical microscope image of cPPA photoresist without PAG at exposure dosage of 2.1 J/cm².

To understand the importance of PAG, two photoresists solutions containing cPPA with 20 wt% TPS triflate and aryl tosylate as PAGs were spin coated and post apply baked as described for the lithographic process. The PAG containing cPPA resist systems were exposed on a 254 nm ABM contact aligner. Interestingly, clear patterns were obtained for the resist system containing TPS triflate PAG, even without PEB and further development at an exposure dosage of 1 mJ/cm². This indicates the self-developing nature and high sensitivity of cPPA resist with a strong ionic TPS triflate PAG (pK_a -14). Figure 2.7a, shows the optical microscope image of a pattern observed for the TPS triflate resist system. As discussed earlier, self-developing resist systems are not desired for high volume manufacturing (HVM) as the volatile scission products liberated may contaminate the exposure tools. In contrast to TPS triflate PAG, the resist system containing aryl tosylate PAG generates weaker toluene sulfonic acid (pK_a : -2.8) produced clear patterns when exposed to 20 mJ/cm² dosage and further PEB (70 °C for 60 seconds) and development using 2-propanol (120 seconds). The weaker toluene sulfonic acids produced are sufficient to cause complete depolymerization of cPPA in the exposed regions due to the presence of acetal linkages in the main chain which are sensitive to acids. Figure 2.7b shows the optical microscope image of pattern observed for resist system containing aryl tosylate PAG . We can observe that closely spaced lines have severely swollen and joined structures leading to problem of bridging between the lines upon the removal of the solvent. This could be due to uncontrollable acid diffusions during PEB after photo exposure. The mobility of the activated aryl tosylate PAG has led to excessive diffusion into unexposed areas of the film.



Figure 2.7. Optical microscope images of cPPA resist systems with a) TPS triflate PAG b) aryl tosylate PAG.

2.3.1.4 Role of base quenchers

Acid diffusion in photoresist systems led to critical dimension variations and line edge roughness in high resolution patterning and hence it is important to control the same²⁴. Hence, a series of base additives with varying proton affinities were added to the cPPA films with aryl tosylate PAG as listed in table 2.1 to study the effect of base quenchers in controlling diffusion of acids. Photoresist system of cPPA with 20 wt% aryl tosylate PAG (with respect to polymer) was used as the base resist matrix and 10 mol% of base quenchers (with respect to PAG) listed in table 2.1 were added to prepare resist solutions. The prepared resist solutions were spin cast and PAB as described in the lithographic process was carried out. A resist solution containing no base quencher (BQ) was also studied as a control system.

Table 2.1. Proton affinities and vapor pressures of base quenchers used in experiment²⁶.

Number	Compound	Proton affinity	Vapor pressure
		(kJ/mol)	(mmHg at 20 °C)
BQ1	<i>N,N</i> '-dimethylformamide	884	2.7
BQ2	N,N'-dimethylaniline	935	1
BQ3	Tributylamine	982	0.3

In order to determine the optimal exposure dosage necessary for high resolution patterning, contrast curves were constructed using a flood exposure dose array when exposing these resist systems at 248 nm ASML DUV projection lithography. The PEB and development process are carried out as stated above, and the film thickness at each exposure dosage is measured with a P10 Profilometer. From the contrast curves in Figure 2.8 the minimum dose to clear all the resist at the exposed area was determined. The effect of exposure dosage on the normalized thickness is highly pronounced in the resist system containing BQ3. On the other hand, addition of BQ1 or BQ2 to the resist system has negligible effect on the contrast curve when compared to resist systems with no BQ.

This could be due to a combined effect of two factors - proton affinity and vapor pressure of the base quenchers. Among the three base quenchers, BQ3 has the highest proton affinity leading to most effective quenching of protons from the generated acids. Cyclohexanone, which is used as the solvent of a resist solution has a vapor pressure of 5 mmHg at 20 °C. This solvent vaporizes during the process of spin coating and PAB, leaving behind a homogenous film for exposure. The base quenchers, BQ1 and BQ2 have vapor pressures comparable to cyclohexanone as listed in table 2.1. This leads to a hypothesis that the BQ1 and BQ2 could have potentially vaporized along with the cyclohexanone during spin casting and PAB. BQ3 on the other hand has a vapor pressure much lower than that of the other two base quenchers and hence contributing negatively to acid diffusion.

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Figure 2.8. Contrast curves for resist systems containing no BQ, BQ1, BQ2, BQ3.

2.3.1.5 DUV projection lithography

To understand the effect of BQ on the imaging quality, resist systems containing the resist matrix (cPPA and aryl Tosylate PAG) and the base quenchers listed in table 2.1 were prepared and patterned with the 248 nm ASML DUV projection lithography as described in the lithographic process. Each wafer had a coating thickness of 55 nm and was processed identically. The DUV exposure mask used in this experiment consists of 512 nm 1:1 line and space patterns. The exposed wafers were subjected to PEB at 70 °C for 60 seconds followed by non-aqueous development with 2-propanol for 120 seconds.

Figures 2.9-2.11 show the AFM analyses of the resist matrix containing no BQ, BQ2 and BQ3, respectively. The resist matrix containing BQ1 (N,N'-dimethylformamide) showed similar performance as BQ2 (N,N'-dimethylaniline) and therefore the results of which are not discussed in this chapter.

512 nm 1:1 line space patterns were observed for resist systems with no BQ, BQ2 and BQ3 at 20 mJ/cm², 30 mJ/cm², and 100 mJ/cm², respectively. From the phase retrace images in Figures 2.9- 2.11 two distinct phases were traced by the AFM – one phase representing the exposed region and the other unexposed region. This indicates complete development of the resist on the substrate in the DUV exposed regions.

From the height retrace and cross sectional profile in Figure 2.9 and Figure 2.10 a similar performance of the cPPA resist systems with no BQ and BQ2 in terms of profile shape and exposure dosage requirements was observed. This further supports the hypothesis that the absence of BQ2 in resist systems during exposure, could have led to no quenching of the gnerated acids. The phase retrace images in Figure 2.9 and Figure 2.10 also indicates that there could be residual scissioned products at the exposed regions.

Among the three resist systems, resist system containing BQ3 (tributylamine) showed superior lithographic perfermance (Figure 2.11). From the height retrace and cross sectional profiles, the diffuion

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of acid is reduced BQ3 leading to sharpening of the image slope and improved profile shape. The phase retrace image in Figure 2.11 also indicates no residual chain scission products in the exposed areas. We thereby understand that the reaction of acids with base quenchers is essential for controlling acid diffusions in cPPA resist systems. The addition of BQ in the resist system has clearly enhanced the imaging properties, but at the expense of higher exposure dosage requirements, taking us back to the RLS (resolution- LER- sensitivity) tradeoff discussed in chapter 1.



Figure 2.9. AFM images of a) height retrace b) phase retrace and
c) cross sectional profile of cPPA resist system containing no BQ
exposed at 20 mJ/cm² DUV radiations.



Figure 2.10. AFM images of a) height retrace b) phase retrace and c) cross sectional profile of cPPA resist system containing BQ2 exposed at 30 mJ/cm² DUV radiations.



Figure 2.11. AFM images of a) height retrace b) phase retrace and c) cross sectional profile of cPPA resist system containing BQ3 exposed at 100 mJ/cm² DUV radiations.

2.3.1.6 Scanning electron microscopy

In order to further characterize the DUV exposed resist systems, scanning electron microscopy (SEM) and focused ion beam scanning electron microscopy (FIB-SEM) were used. SEM is considered to be the industry standard for characterization in HVM and for measuring critical dimension and LER in defect analysis²⁷. Based on our understanding from AFM analysis, we characterized the resist system containing BQ3 using SEM. The 512 nm 1:1 line space analyzed using AFM, were sputter coated using s Denton Desk V high vacuum sputter coater available at the CCMR (Cornell Center for Materials Research). A thin layer of conductive metal (Iridium) was deposited onto a wafer fragment for the purpose of removal of charge buildup during SEM imaging.

Figure 2.12a and b shows the SEM and FIB-SEM cross sectional images of the patterned resist, respectively. Attempts to obtain high resolution SEM of the DUV patterned cPPA resist systems were unsuccessful. The unexposed resist decomposes in the microscope due to their high sensitivity towards e-beam radiation. This is not surprising as polyphthalaldehyde based resist systems were first developed for ebeam lithography¹⁵.



Figure 2.12. a) SEM b) FIB-SEM images of the DUV patterned cPPA resist systems containing BQ3.

Another major concern about the cPPA resist systems, is the formation of clear latent images when the resist systems are removed from the DUV exposure tools. This can be observed in all the cPPA resist systems with and without the use of base additive components. This could presumably be due to the outgassing of the volatile scissioned product, o-phthalaldehyde which causes reduction in the film thickness. Outgassing of scissioned products are undesirable as they lead to deposition of organic compounds on lithography tools that can affect the optical properties of the tool and ultimately affect imaging quality²⁸.

2.3.2 Br-lPPA multicomponent photoresist

Controlling the outgassing of resist is critical because of the highly energetic radiation sources in EUV lithography. Outgassing of the scissioned product, o-phthalaldehyde is due to its volatile nature during DUV exposures. Therefore, there is a need to overcome or reduce outgassing problem as we continue to optimize phthalaldehyde based resist systems for EUV lithography. This may be achieved by increasing the molecular weight of the monomer used. To this end, brominated derivative of the monomer, Br-phthalaldehyde was polymerized into, Br-/PPA and Br-cPPA which were used for further lithographic evaluation. Since Br-cPPA was found to have a shelf life much lower than that of Br-/PPA, further studies were carried out used the latter.

2.3.2.1 DUV projection lithography

To understand the role of BQ in the resist matrix containing Br-*l*PPA and aryl tosylate PAG, lithographic evaluation was performed using 248nm DUV projection lithography. Multicomponent resist systems containing Br-*l*PPA, aryl tosylate PAG, and tributyl amine (BQ) were prepared and identically spin cast as described in the section on lithographic processing and had a film thickness of 50 nm. Further, they were patterned with 248 nm ASML DUV projection lithography using 512 nm 1:1 line and spaced exposure masks as described in the lithographic process. The exposed wafers were PEB at 70 °C for 60 seconds followed by development with 2-propanol for 120 seconds. Figures 2.13 and 2.14 show the AFM analyses of the Br-/PPA resist systems containing no BQ and BQ, respectively. Clear patterns were observed at 135 mJ/cm², and 200 mJ/cm² for the Br-/PPA resist systems with and without BQ.



Figure 2.13. AFM images of a) height retrace b) phase retrace and c) cross sectional profile of Br-lPPA resist system containing no BQ exposed at 135 mJ/cm² DUV radiations.



Figure 2.14. AFM images of a) height retrace b) phase retrace and c) cross sectional profile of Br-IPPA resist system containing tributylamine exposed at 200 mJ/cm² DUV radiations.

From the height retrace and cross sectional profile images from Figure 2.13 and Figure 2.14, a similar performance of the Br-*l*PPA resist systems with and without BQ in terms of profile shape and LER was acheived. Notably, the photospeed of the latter is much higher than the former because of the absence of base quencher in the resist system. A higher photospeed is desired especially for HVM because of lower energy requirements in fabrication process.

However, despite the absence of BQ in Br-/PPA resist system, the exposure dosage requirement was higher (135 mJ/cm²) in comparison to cPPA resist systems (100 mJ/cm²) containing BQ3. This could be explained due to the restricted mobility and resulting confinement of generated acid in the Br-/PPA matrix during DUV irradiations because of the higher molecular weight Br-/PPA scissioned products. This leads to an increase in overall demand for the generated acids in the exposed

regions and this requirement is met by absorption of more photons in the exposed regions resulting to an increase in exposure dosage.

2.3.2.2 Scanning electron microscopy

Figure 2.15 shows the SEM image of Br-*l*PPA resist system containing no BQ exposed at 135 mJ/cm² DUV irradiations. The resist system was deposited with a thin layer of Iridium as conductive layer to avoid charge buildup during SEM characterization. The DUV patterned resist system was stable, and we observed no decomposition of the unexposed resist during SEM imaging.

Also, the Br-/PPA based multicomponent resist system has successfully resolved the issue of formation of latent images during DUV exposures. No latent images were observed when the resist systems were removed from the DUV exposure tools. This could be due to the higher molecular weight of scissioned products of Br-/PPA, which are less volatile compared to scissioned products of cPPA.



Figure 2.15. SEM image of the DUV patterned Br-lPPA resist systems without BQ.

2.3.2.3 Contrast curve

The DUV patterning results of Br-/PPA containing aryl tosylate PAG, indicates that the resist system has a very poor sensitivity of 135 mJ/cm². This could be due to several reasons – poor absorption of PAG at DUV wavelength or poor acid generation efficiency. Therefore, contrast curves were studied for a series of photoacid generators PAG 2-6 using a flood exposure dose array at 248 nm as described in lithographic process. The resist system containing aryl tosylate PAG was also studied as a control system to compare the sensitivity of other PAGs. Each photoresist spin casted wafer had a coating thickness of 55 nm and was processed identically. Resist systems containing PAG1 to PAG-5 was PEB at 60 °C for 60 seconds while the resist system with PAG6 was PEB at 60 °C for 30 seconds. Figure 2.16 shows all the PAG structures used in this study.



Figure 2.16. Chemical structures of all the PAGs used in this study.

From the contrast curves shown in Figure 2.17, Br-/PPA resist systems containing napthalamide tosylate (PAG6) has the highest sensitivity compared to any other PAG investigated in this study. The minimum dose required to clear all resist for the resist system containing PAG6 was 20 mJ/cm². No latent images were observed when the exposed resist was removed from the DUV exposure tool. The highly sensitive nature of resist system containing PAG6 can be explained due to the presence of nitroxide bonds in PAG6 which are more unstable to UV irradiations. Also, the presence of additional benzene and bromine in the PAG6 structure will lead to an increased absorption of DUV radiations. The activated PAG generates a bulkier anions/cations compared to the other PAG 1-5. This will reduce diffusion of the acid as the generated acid cannot diffuse through the resist matrix as easily as before due to their restricted mobility owing to their larger size.



Figure 2.17. Contrast curves of Br-lPPA resist systems containing a PAGs.

The Br-*l*PPA resist system containing PAG6 demonstrates a very sharp contrast curve while in case of other resist systems we see that the development rate of the resist systems increases only linearly with the exposure dose. Sharp contrast exposure behavior in photoresists is a desired property for high resolution patterning due to the very low erosion of weakly exposed areas and their ability to develop at a constant and high rate from a specific light dose.
The results from Br-/PPA resist systems containing PAG6 show promising results for high resolution patterning due to their high sensitivity, high contrast and non-volatile nature of the scissioned products during UV light exposures.

2.4 Conclusions

Lithographic studies were carried out to evaluate potential EUV photoresists based on PPA with PAG and BQ. The multicomponent resist systems containing derivatives of PPA combined with PAG and BQ showed good solubility in common solvents and homogenous film formation. We explored several ionic and nonionic PAGs and evaluated the role of photoacid generation in improving the sensitivity of the PPA photoresist. PPA photoresists with strong acid generating TPS triflate PAG exhibited self-developing nature while clear patterns were obtained for PPA photoresists combined with weaker acid generating aryl tosylate PAG upon post exposure baking and development.

Photoresist systems containing cPPA and aryl tosylate PAG indicated uncontrolled acid diffusions in unexposed regions due to the mobility of generated acids during UV exposures. Tributylamine as BQ was introduced as an acid quenching additive to the cPPA resist system which played a significant role in controlling acid diffusions resulting in improved lithographic performance. However, the cPPA resist system produced latent images during DUV exposure. Also, the unexposed cPPA resist decomposed during SEM imaging due to its high sensitivity towards electron beam radiation. These problems were successfully countered by the Br-/PPA resist systems due to the increased molecular weight of the corresponding Br-/PPA scissioned products which are less volatile compared to scissioned products of cPPA.

Br-/PPA resists containing aryl tosylate PAG showed promising results in terms of profile shape, LER even without the influence of BQ but at the expense of higher exposure dosage. No latent images were observed in the DUV patterned Br-/PPA resist systems and were stable to SEM characterizations. Further, a series of PAGs with Br-/PPA were investigated to improve the sensitivity of Br-/PPA photoresist. The resist system containing napthalamide tosylate PAG exhibited desired photosensitivity and a sharp contrast curve compared to other PAGs. In order to achieve higher resolution patterning, we continue to evaluate the Br-/PPA photoresist system combined with PAGs using 13.5 nm EUV lithography.

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CHAPTER 3

COMPLEMENTARY WORK AND FUTURE GOALS

3.1 Introduction

The primary goal of this thesis is to design a photoresist for Extreme Ultraviolet (EUV) lithography. The photoresist system containing Br-/PPA and PAG was extensively studied using Deep Ultraviolet (DUV) lithography in chapter 2. The DUV lithographic performance of the Br-/PPA multicomponent resist system showed promising results in terms of profile shape and line edge roughness. These results indicate that there is a great potential of using Br-/PPA resist system for 13.5 nm EUV lithography. In this chapter, we discuss the preliminary evaluation of Br-/PPA resists system using EUV flood exposure, the results of which support the idea of investigating polyphthalaldehyde as a potential EUV photoresist.

The lithographic evaluation of the multicomponent photoresist system containing Br-*l*PPA and PAG showed a significant loss in film thickness after DUV exposures followed by non-aqueous development. This could have a detrimental effect on high resolution patterning (<10 nm) leading to resist pattern collapse. Researchers from other groups have previously reported that the inhomogeneous PAG distribution in

^{*}The concept of single component photoresist system containing aryl tosylate PAG tethered to Br-*l*PPA was adapted from Jingyuan Deng, Ober research group, Cornell University.

multicomponent resist systems could be a potential reason behind the loss in film thickness^{1-2,4}. Herein, we discuss the possibility of a single component resist system where the PAG is covalently bound to the main chain of the polymer to resolve this issue.

3.2 EUV lithography

Lithographic evaluation of the Br-*l*PPA resist system containing PAGs showed promising results with DUV projection lithography. In order to achieve higher resolution patterning of features (<10 nm), the resist systems were further evaluated using EUV lithography.

3.2.1 Lithographic procedure

A photoresist system of 5 wt% Br-IPPA with 20 wt% PAG (with respect to polymer) was added to cyclohexanone to prepare the resist solutions. Three PAGs as shown in Figure 3.1 were evaluated in combination with Br-IPPA resist systems using the EUV flood exposure tool at Intel, Oregon. The resist solutions were spin-coated and PAB at 90 °C for 60 seconds. The resist system containing aryl tosylate (PAG1) was subjected to PEB at 60 °C for 30 seconds while resist systems containing TPS triflate (PAG2) and NpN triflate (PAG3) were PEB at 100 °C for 30 seconds. All the wafers were processed identically and were developed by 2-propanol for 60 seconds.





Aryl tosylate (PAG 1)

TPS triflate (PAG 2)



NpN triflate (PAG 3)

Figure 3.1. Chemical structures of PAGs.

3.2.2 Results and Discussions

From the contrast curves shown in Figure 3.2, we determine the minimum dose to clear all resist using EUV flood exposure. The resist system containing PAG1 showed a linear development rate with increasing exposure doses, while resist systems containing PAG 2 and 3 showed a very sharp contrast. The resist system containing PAG3 has the highest sensitivity and hence, these results are consistent with the DUV contrast curves discussed in chapter 2 (refer to Figure 2.17).



Figure 3.2. Contrast curves for Br-lPPA resist systems containing PAGs.

3.3 Top layer loss

The DUV lithographic evaluation of the Br-/PPA resists systems containing PAG were discussed earlier, in chapter 2. From the AFM analysis of the 512 nm 1:1 line spaced patterns (Figures 2.9- 2.11 and 2.13- 2.14), we suspect that there could potentially exist an issue of top layer loss. The height retrace and corresponding cross sectional profile of a Br-/PPA resist system containing aryl Tosylate PAG and no BQ, exposed to 135 mJ/cm² DUV radiations is shown in Figure 3.3. The initial thickness of the resist film before exposure was measured to be 50 nm. However, from the cross sectional profile shown in Figure 3.3b, the measured height of the DUV exposed line patterns is ~35 nm. The loss in film thickness after DUV exposure followed by non-aqueous development is observed in all the DUV patterning results discussed so far.



Figure 3.3. a) height retrace b) cross sectional profile of BrlPPA resist system.

This may be due to the inhomogeneous distribution of PAGs in the photoresist. Multicomponent resist systems are composed of a polymer matrix, photoacid generator (PAG), and base additives; the homogeneity of this blend is a critical factor influencing ideal pattern forming capability of the resist¹⁻⁴. It has been reported that most PAGs in multicomponent systems tend to aggregate and phase separate from the resist matrix⁵. The polarity of PAG molecules was reported to be one of the major factors affecting the local density variations near surface and interface⁴. This could lead to the inhomogeneous vertical distribution of PAG resulting in the enrichment of PAGs near the surface of the photoresist. Therefore, we hypothesis that the top layer

loss could potentially be due to the localized effect of concentration of PAGs on the photoresist surface. In fact, it has been previously reported that the effect of local inhomogeneity in vertical PAG distribution could be the reason for poor pattern formations such as top-rounding and footing⁵.

3.4 Single component PPA photoresist

The inhomogeneous distribution of PAGs also contributes to a stochastics variation within photoresist. Stochastic variations occur inside the photoresist due to the photoelectric and molecular reactions during UV exposure⁶. The EUV photons from the light source interacting with the resist molecules (primarily PAGs) are only available at discrete locations in limited numbers. This leads to local inhomogeneity i.e., variations in the probability of the number of photons interacting with the number of PAGs within the exposed regions of photoresist. The stochastic effects are considered to be one of the important limiting factors in the application of EUV as it could have adverse effects on critical dimension variability (LER). Figure 3.4 shows an illustration of an ideal photoresist with uniform PAG distribution compared to a photoresist involving PAG aggregation and inhomogeneous distribution.



Figure 3.4. graphical illustration of a) homogenous distribution of PAG in ideal photoresist b) inhomogeneous distribution of PAG in real photoresist².

A new class of single component multifunctional photoresist is extensively studied to tackle the issue of stochastics. The single component system consisting of a photoacid generator which is covalently bound to the main chain of the polymer has gained significant attention in recent years⁷. Polymer-bound PAGs have a significant advantage over multicomponent resist systems that can potentially help in satisfying the RLS tradeoff. Unlike multicomponent systems, they have no physically blended additives such as PAG and BQ, ensuring a homogeneous resist film. These systems also give the possibility for very high PAG loadings, which further improves the sensitivity of the photoresists. Hence, we propose that the PAG tethered Br-*I*PPA resist system could potentially help in solving the issue of top layer loss due to the homogeneous distribution of PAGs in the resist matrix. The Ober research group is currently focusing on the synthesis of Br-*l*PPA bound PAG single component resist systems as shown in Figure 3.5.



Figure 3.5. Aryl tosylate PAG tethered to Br-lPPA.

3.5 Future goals

In this work, preliminary EUV evaluation of the multicomponent Br-/PPA resist system with three different PAGs was studied. The results from the EUV contrast curve indicate similar lithographic performance as compared to DUV flood exposures in terms of the photosensitive nature of resist systems containing Br-/PPA and PAGs of varying acid strength. This motivates us to further investigate the potential of Br-/PPA as a EUV photoresist for high resolution patterning. Based on the DUV lithographic evaluation of the multicomponent photoresist systems discussed in this thesis we may expect similar top layer loss due to the inhomogeneous PAG distributions in EUV patterning. To overcome this issue, we should continue to focus on the design of single component PAG tethered Br-/PPA photoresist system.

Our collaborators from the Escobedo research group are currently conducting atomistic molecular dynamic simulations of PAG tethered Br-/PPA photoresists using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). Preliminary results from the simulations indicate that the PAG tethered Br-/PPA system has better spatial distribution when compared to the multicomponent system. These results encourage us to further analyze the single component systems.

The next steps in designing a EUV photoresist based on PAG tethered Br-/PPA systems should focus on obtaining high resolution patterns (<10 nm) while simultaneously satisfying the industry set requirements for sensitivity and line edge roughness. Experimental optimization will be required in choosing the ideal PAG loading and processing conditions such as EUV exposure dose, post exposure baking, and nonaqueous development conditions.

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