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Characterization of 157 nm photoresist materials for advanced lithographic processess

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**CHARACTERIZATION OF 157 nm PHOTORESIST MATERIALS FOR
ADVANCED LITHOGRAPHIC PROCESSES**

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

San Jose State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

By

Nasim Gholizadeh

May 2006

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ABSTRACT

CHARACTERIZATION OF 157 nm PHOTORESIST MATERIALS FOR ADVANCED LITHOGRAPHIC PROCESSES

By Nasim Gholizadeh

Lithography and photoresist are key components for high volume production (HVM) of integrated circuits. The difficulty in understanding the lithography process lies in the fact that many factors such as optics, photoresist chemistry, processing conditions, etc. can affect the outcome of the lithography process. In HVM resist is subjected to harsh processing conditions. Thus, properties of the photoresist can be irreversibly changed affecting the performance of the resist and quality of the lithographic process.

In this study, chemical and thermal properties of 157 nm chemically amplified (CA) resist were characterized by investigating the specific roles of solvent, backbone resin and photoacid generating compound (PAG). Additionally, the effect of substrate and resist interactions was evaluated. For the system of resists studied, results suggest that solvent and polymer effects dominate the thermal and chemical properties of the resist. It was also determined that resist properties are independent of substrate and PAG molecule.

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CHAPTER 1

INTRODUCTION

Since its invention in the 1950's, integrated circuits (IC) manufacturing has significantly altered global advancement and technological innovations [1]. The advancement of the semiconductor industry has been made possible by 25-30% declining cost per function of integrated circuit per year due to improved process and equipment performance [2].

Regardless of the numerous advancements made in the semiconductor industry, this technology sector faces many challenges. Among the many processing steps, lithography has emerged as one of the most critical, costly and technically challenging processes in the IC manufacturing. Advancing technology and growing microprocessor complexity require tools that can process material without damaging the underlying surface and durable materials that can stand harsh processing conditions. These limitations require the collaboration of multiple disciplines to gain a competitive business edge. It is because of these limitations that the ability to understand the role of resist chemistry is gaining more importance.

In the lithography process, properties of surface layers and their interaction with resist material affect the behavior and durability of the resist [3]. Interfacial effects modify the properties of the bulk chemistry and therefore the interaction of the material with the substrate. This creates a micro-molecular layer with dissimilar properties. The presence of this layer transforms the properties of the polymer [3]. Learning about the

arrangement of the molecules on the surface layer and the mechanisms responsible for creating these micro and macro interfacial effects are of great importance. Gaining this knowledge will enable the existing technology to meet aggressive lithography requirements not only through equipment and mask design modifications but also through chemistry improvements [2].

Besides technological contributions, there are also cost factors driving the lithography innovations. In 2002, there were more than 200 lithographic operations conducted for 8" wafer in an IC manufacturing process [2]. Consequently the market size for lithography material is expected to increase from \$8 billion in 2002 to \$25 billion in 2005 [2]. It is projected that the associated cost and the number of operations in IC manufacturing will increase significantly by introduction of Deep EUV processes for 65 nm DRAM technology [4]. Despite the market growth and innovations in IC manufacturing and lithography, resist engineering remains one of the least comprehended areas of IC manufacturing process.

As described above, the effect of chemical interaction and material organization on the substrate is critical and may be a technology enabling science for future of semiconductor industry. Consequently, a study was proposed with the aim to understand the effect of chemistry and surface interaction on different substrates. The study further investigated the effect of various components in the resist on the overall performance of the material.

CHAPTER 2

BACKGROUND INFORMATION

As scaling down in device size continues to drive the technology innovations, establishing lithography science capable of meeting aggressive technology goals becomes crucial [5]. Highly complex resist materials combined with advanced optical manufacturing tools has allowed the industry leaders like Intel and IBM to fabricate 100 nm features. Significant technical obstacles bring uncertainties to the future of semiconductor industry [6]. Therefore, it is critical to be able to develop new materials to achieve a successful lithography process that consistently produces defect free film characteristics [7].

2.1 General Overview of Lithography Process

Lithography is a process which combines the science of photoresist exposure and optical processing techniques. Figure 1 illustrates a typical photoresist process flow [1]. In a lithography process, a pattern from a reticle is transferred onto the wafer surface. The transfer of pattern onto wafer is achieved by utilization of photosensitive material called photoresist. Before the application of the resist material, the first step in the lithography process is cleaning the surface of the substrate to improve adhesion followed by a dehydration bake at 150°C-200°C for 15 minutes [8].

Following the dehydration bake, the wafer is exposed to hexamethyldisilazane (HMDS) to prime the surface by removing any moisture. The next step is to spin coat the wafers and expose the wafers to softbake at 100°C-150°C for 2 minutes. This is done to

allow evaporation of solvents and to improve surface adhesion. The last step in the process is exposure to light source and development of the resist material [8].

Figure 1: Typical Photoresist Process Flow [8].

There are two types of resist used in lithography process: positive and negative resist, as shown in Figure 2. In the case of positive resist, exposed areas are removed in the subsequent steps. Whereas in the case of negative resists the opposite is true; the exposed areas are polymerized and become hard [8]. Upon completion of the lithographic process, the wafer is sent for subsequent processing steps. The wafer ultimately returns to the lithography process in preparation for further processing.

Figure 2: Schematic Presentation of Positive and Negative Resist Process [8].

2.2 Overview of Lithography Chemistry

Photoresist is a photosensitive material that changes its physical and chemical properties when exposed to light. In general, photoresist materials consist of three major components: an inactive hydrocarbon backbone polymer chain, a photoactive compound (PAC) which is made of a hydrocarbon chain responsible for inhibiting dissolution of resist in developer and a solvent functional group used to control the viscosity of the resist material [1]. Table 1 represents various polymer structures used in different lithographic techniques.

In the early 1980's, common resists consisted of novolac resin and photoactive diazonaphthoquinone dissolution inhibitors. The resist was processed with deep-UV lithography utilizing a KrF excimer laser (248 nm). The performance of this chemistry and wavelength combination was not adequate to meet technology requirements due to the high rate of absorption of these materials at this wavelength. Simply said; the mechanism in the resist which was responsible for initiating a reaction instead inhibit the reaction by absorbed the active photons. This prevented penetration of the photon through the full thickness of the resist and resulted in under developed resist profiles that did not meet industry standards [1].

As a result, the resist system used in ArF (193 nm) excimer laser lithography was developed. This technology was also facing similar limitations and therefore the platform polymer had to be altered from an aromatic to aliphatic structure to meet transparency requirements. Finally, the continuing search for higher resolution at shorter wavelengths initiated a massive attempt to develop chemical amplification resists for use

at 157 nm (F_2 excimer laser) wavelength. Development of these different resist materials for various wavelength technologies has been crucial to meet objectives of each technology node [9].

Table 1: Polymer Structures Used in Different Lithographic Techniques [9].

i-line 365 nm	DUV 248 nm	ArF 193 nm

0.02 /μm	0.18 /μm	0.22 /mm
F_2 157 nm	EUV 13.4 nm	X-ray 1 nm

2.35 /μm	1.55 /μm	0.12 /mm
100 kV E-Bea	75 kV H^+, He^+ Ion Beam

0.02 /μm	3.7 /μm	

2.3 Background Information on 157 nm Resist Material

In order to engineer devices with critical dimensions of 100 nm or less, a new set of engineering and infrastructure requirements must be satisfied. Presentation of 157 nm lithography in IC manufacturing process requires development of new laser wavelength, mask and photoresist materials. Although all aspects of this infrastructure are under development, there has been increasing concern for meeting these technology requirements [10].

A recent survey conducted by SEMATECH showed that the most significant obstacle for enabling 157 nm technology was developing photoresist material (Figure 3)

[4]. The source of these concerns is well founded considering that newly developed materials have many limitations. For example, key substances such as O₂, H₂O and some of the commonly used polymer platforms strongly absorb at 157 nm wavelength. Furthermore, simple modification of existing hydrocarbon resist does not lead to enough improvements to meet the requirements of 157 nm technology [1].

Figure 3: Survey Results of Microlithography Subcomponent Process, SEMATECH. Survey Conducted at Next Generation Lithography Review: Higher Score Indicates Confidence that the Technology can Meet the SIA Roadmap [4].

The search for materials that can overcome these challenges is driving continuing pursuit for higher resolution at shorter wavelengths. These requirements have recently encouraged developing a new series of resists for use at 157 nm (F₂ excimer laser) [11, 12]. The newly founded materials are based on a mechanism called chemical amplification.

Chemically amplified (CA) resist is based on a photo acid generation (PAG) reaction mechanism. Figure 4 illustrates the basic chemical reaction mechanism for CA

resist. As shown in Figure 4 (a), the incoming photons and PAG molecules react creating acid molecules. During a subsequent bake step in the process (4b), the newly generated acid molecules act as reaction catalysts and change the properties of the resist.

Figure 4: Reaction Mechanism for Chemically Amplified Resist [1].

In the case of the positive resist, the PAG molecule initiates a chemical reaction which makes the resist molecules soluble in the presence of the developer (4c). As shown in (4d), since the reaction is catalytic, the acid molecules are continuously regenerated after completion of each reaction. As a result of this mechanism, they contribute to further chemical reactions, thus improving on some of the limitations of the previously used resist materials [1].

CHAPTER 3

LITERATURE REVIEW

In the past years, due to optical performance requirements and reliability issues facing IC manufacturing, significant investments in research and development have been made. However, most of the work that has been done is with respect to exposure and imaging technology requirements. Although most recently, to meet the challenging requirements of lithography, material characterization studies have increased, the complex science of resist material requires additional studies to further the existing body of knowledge [9].

In previously conducted research, the chemical composition of some of the most commonly used resists for 248 nm and 193 nm wavelengths have been characterized [13]. However, since the chemical properties of the materials used at these wavelengths are significantly different than the chemical properties of 157 nm resist, the current industry research goal is to generate similar thermal and chemical data for resist materials that will be used for 157 nm wavelength. This review summarizes the key findings from previously conducted studies on 193 nm and 248 nm resist properties with an aim to investigate possible opportunities for cross learning.

3.1 Temperature Analysis

Numerous papers have investigated the thermal stability of resist materials since changes to individual components of the resist will profoundly affect the performance of the lithographic process. In general, the resist material has amorphous properties. The

physical properties of resist material are established by molecular movement of individual molecules [7].

During processing, the molecular motions of the resist components depend on temperature changes. As the temperature increases, the molecular movement of molecules increases. Eventually the molecules reach a steady state as they approach their glass transition temperature (T_g). At the glass transition temperature, the amorphous properties of the polymer change their characteristic to glassy and brittle.

The glass transition temperature affects many properties of photoresist material such as adhesion, hardness, tackiness. The various bake steps in IC manufacturing process is determined by material glass transition temperature. For a chemically amplified resist, the main parameter that defines various bake steps and identifies performance of the material under harsh processing conditions (i.e. shrinkage of CD due to thermal processing) is glass transition temperature. Therefore materials with high T_g are desired. [14].

It is critical to understand the thermodynamic properties of various resist materials to enable 157 nm technology to meet critical dimension and other device requirements. The two most commonly used methodologies to thermally characterize the CA resist material are Modulated Differential Scanning Calorimetry (MDSC) and Thermo-Gravimetric Analysis (TGA).

Jui-Hsuang Liu investigated the effect of PAG on thermal stability of the resist formulations of various polymer and PAG combination by applying MDSC. Three positive tone resist consisting of carboxyl PAG functional group was studied. Scientists

looked at resist polymers with and without PAG molecules. The formulations were exposed to UV light and then were treated at 180°C. The authors related the weight loss to thermal stability of the material. Figure 5 shows that below 200°C thermostability of the polymer with and without PAG was not much different. However at temperatures above 200°C, significant variations in thermal properties of resist materials were observed. The author concluded that at high temperatures the existence of carboxyl groups will increase chemical interactions causing a stronger presence of attractive and repulsive forces to exist. These forces will limit the mobility of the polymer chains resulting in improvements in the thermostability of the resist material [14].

Figure 5: Effect of Carboxyl Functional Group on Thermostability of Copolymers without any PAG Molecules: (1) Copolymer 1 without Carboxyl Functional Group, (2) Copolymer 2 with Higher Than 25% Carboxyl Functional Group, (3) Copolymer 3 with 25% Carboxyl Functional Group [14].

In an experimental study conducted by F. Seyedi, scientists investigated the effect of resin polymer on the thermal stability of the resist. The study included Novolak resin resist materials for 248 nm exposure wavelength. Scientists developed different Novolak resist mixtures with controlled molecular weights. In order to characterize the material they increased molecular weight of the solution [15]. They exposed the formulated material to thermal scan that was carried out at 2°C/min up to 200°C.

The Novolak resins produced a T_g that ranged from 120°C to 130°C with slow dissolution rate. To improve the dissolution rate of the Novolak resin, they introduced an ester functional group that increased the molecular weight of the polymer. After repeating the thermal testing, they observed an increase in the glass transition temperature that ranged from 140°C-150°C. In conclusion of this analysis, the scientists determined that increasing molecular weight of the platform polymer will increase steric hindrance resulting in more thermally stable materials with higher glass transition temperature [15].

In a study conducted by Park, he applied TGA to study chemically amplified resist materials for next generation lithography. A resist solution was prepared by dissolving 1g of a non disclosed polymer and 0.02g of thirphenylsufonium as a PAG. By varying the polymer, three different formulations were prepared [16].

The different formulation solutions were spun on Si wafers and exposed to g-line exposure tool. Later the film was exposed and baked at 140°C for 2 minutes. The prepared polymers were analyzed by conducting TGA analysis. The intention of the study was to investigate the kinetic phenomena that govern the crosslinking reaction.

The conducted study indicated that as the molecular weight of the starting polymer and the temperature increased the volume of aggregates that made up the film increased. They concluded that as temperature increased the percentage of crosslinking groups increased [16].

3.2 Mechanical Analysis

3.2.1 Contact Angle Analysis

The effect of substrate properties and their interactions with the materials that they come in contact with in sequential steps have a profound effect on film characteristics. For example, surface uniformity of the resist and planarization depend on the surface tension of the materials involved in the lithographic process. Thus far, most of the conducted studies have focused on evaluating and modifying complex properties of chemically amplified resist for i-line and g-line exposure systems by applying NMR, SEM, AFM and contact angle (CA) analysis.

In one such study, J. Bauer and G. Drescher studied surface properties for various systems of different substrates (Si, SiO₂, Si₃N₄) and resist material combinations by performing contact angle measurement. In this study, the generated data indicated that the polar surface of Si, SiO₂, Si₃N₄ are extremely hydrophobic but not significantly different from one another (for the material and substrate combination) [17].

Bauer and G. Drescher also looked at modified Si, SiO₂, Si₃N₄ substrates and resist interaction on the surface. After treating the substrates with a primer, there were no apparent differences in the physical properties of the various substrates. This observation may indicate that similar surface properties are achievable by reduction or generation and

stabilization of the surface tension properties for substrates [17]. However, since the substrate performance varies and depends on particular polymer system, it is premature to downplay the effect of substrate on mechanical properties of the resist.

In a different study, K. Part studied effect of resist material and its impact on properties of various systems via static contact angle measurements. They synthesized different formulations of polymers that varied in molecular weight and density. Various substrates (SiO_2 , SiO , SiON) were coated with formulated materials. For all the combinations of resist and substrates, their results showed that the surface wettability is directly proportional to polymer molecule chain density. As a result of their work, the scientists concluded that reorientation of surface polymer chains can influence surface properties such as topography and wettability [16]. This observation shows that by controlling the density and orientation of the chemical functional groups on a molecular level, scientists can manipulate impulsive and repulsive forces that influences surface properties.

Other researchers utilized contact angle methodology in characterizing commercially available 365 nm positive resist manufactured by Shipley on Al sputtered wafer surface by trying to minimize surface forces on the substrates. In this research, the scientists concluded that increasing the molecular weight of the polymer will affect the contact angle parameters such as surface tensions [18]. One way the surface tension will be impacted is that the long polymer chains are flexible and therefore assumed to freely move and rearrange themselves. By rearranging themselves, they will create three

dimensional structures, which will result in areas with low and high repulsive and attractive forces. This formation is believed to contribute to contact angle parameters.

3.3 Performance Analysis

3.3.1 Line Edge Roughness (LER)

As IC manufacturing industry implements shrinking submicron features, it is becoming critical to investigate material sources of defects and technology hindering limitations. One of the biggest limitations of next generation lithography is in the area of resist performance to meet line edge roughness requirements. Line edge roughness (LER) remains a significant challenge due to decreasing feature size and increasing complexity of the resist material.

As the name suggests, line edge roughness is irregularities at the edge or on the sidewall of the features on a device (Figure 6). In general the exact cause of LER is unknown however there are multiple theories to rationalize the source of LER. Most commonly known theories indicate materials and phenomenon that govern their properties to be one of the main sources of LER.

One commonly investigated theory is based on formation of large polymer clusters that dissolve at a lower rate than the bulk polymer. Another theory is based on phase separation of the protected and unprotected polymers [3]. Although it is not possible to identify a primary contributor to LER, the main focus of this paper will be on photoresist material contributions.

Figure 6: An Example of Line Edge Roughness [3].

3.3.1.1 Material Roughness

A number of papers have concluded LER to be due to formation and dissolution of the polymer aggregates. Aggregates are polymer molecules that become entangled either due to their size, density or chemical force. General studies have shown that the surface morphology of a resist can consist of structures that are rough with a granular morphology on top surface, the sidewalls and the cleaved surfaced of a structure [19].

In one such study, Yamaguchi studied LER by investigating the concept that LER is attributed to formation of granular morphology and the magnitude of the LER was related to size of the individual granule. Based on the conducted study, Yamaguchi concluded that LER is due to various sizes of aggregates. She further concluded that these aggregates consisted of entangled single polymer molecules. After the aggregates were formed and the polymer was exposed, the aggregates resulted in nonuniform

dissolution of the exposed polymer. As shown in Figure 7, researchers claimed that in the development process, the exposed regions of the polymer surrounding the aggregates dissolved quicker than the denser polymer aggregates. As a result, aggregates remained surrounded in the surface until most of the polymer in near proximity was removed. After this process, some of the aggregates were extracted from the surface and some remained in place. This process produced surfaces with varying roughness [19].

Figure 7: Dissolution of polymer with aggregates as a function of increasing development time: The polymer surrounding the aggregates undergoes dissolution more rapidly than polymer aggregates [19].

A number of studies indicate that a possible source of LER is due to phase separation of protected and unprotected polymers. In a study conducted by Lin and his colleagues, the effect of solvents, photoacid generator, and base additives on the surface roughness of the films was studied. The study was conducted by investigating fully protected polymers and blends of protected and unprotected polymers [20].

Scientists observed that films with 100% protected and films with 100% unprotected polymers have smooth surface properties, whereas blends of protected and

unprotected polymers showed extremely rough surfaces. The scientists attributed their observation to phase separation of protected and unprotected polymer properties [20].

However, since at the interface, where LER is commonly observed, individual polymer molecules will probably not be completely protected or unprotected. Lin expanded the scope of his study to include films of partially protected and unprotected films. His observations revealed that although very little roughness was seen at 0% unprotection, the roughness significantly increased with an increase in unprotection level of partially protected polymers. The study further confirmed that the observed results of various surface roughness might be due to phase separation of the protected and unprotected films. Lastly, Lin concluded that the differences in surface roughness might be due to the difference in the rate of dissolution of the films with varying levels of unprotection [20].

3.3.1.2 Polymer Backbone

In numerous papers, it has been proposed that LER is highly dependent on polymer backbone structure and significant changes in the level of LER can be accomplished by minute changes in polymer backbone. In one study, scientists analyzed photoresist formulations based on a hydrogen silsesquioxane polymer by conducting SEM analysis. They observed various sizes of aggregates throughout the film. When a polymer with lower molecular weight was used, significant reduction in the size and amount of these aggregates were observed. The result of this study indicated that reduced molecular weight of the polymer reduced the size of polymer aggregates which in return reduced LER [21].

The experimental work done by Brainard and his team resulted in a similar conclusion with respect to LER and material properties. Three different samples of resist with different base materials was studied [22]. The materials considered for this study were three positive resists that varied in molecular weight ranging from 10000 g/mole to 5000 g/mole (XP9947A, XP9947S, and XP9947W). Figure 8 shows a SEM image of the three different resists and the corresponding 3 sigma LER values, which are decreasing proportionally with molecular weight of the polymer resin from 10.2 nm to 7.2 nm to 5.7 nm, respectively. Based on the SEM images and the LER data it has been proven that there is strong dependence of LER on molecular weight of the resist component.

Figure 8: Effect of Molecular dimension of Resin in Resist on LER [22].

However, in a separate study conducted by the same researchers reduced molecular weight did not have a profound effect on LER. The conducted study was based on a “hydrogen silsesquioxane” polymer resist which was investigated with SEM analysis. The data obtained indicated no improvement of LER based on this resist material possibly due to formation of nonlinear molecules caused by attracting chemical forces [22].

In a different study the scientists concluded that a more flexible polymer backbone reduced LER formation. The observations indicated that the flexible polymers were more likely to result in a smooth surface due to easy rearrangement of the molecules during development process. Whereas the more rigid molecules were likely to form three dimensional structures that result in large aggregates [23].

In a second study, the scientist experimented with lowering the polydispersity of the polymer backbone. The results indicated a significant reduction in LER. This might be due to the fact that as the polymers of the same size undergo dissolution at the same rate, all of the polymers at the sidewall are likely to be developed at the same rate, thus resulting in reduced LER [24].

More recently, it has been proven that parameters such as the molecular weight and the polydispersity of polymer backbone influence LER. For example, in one study, Yoshimura suggested that rigid backbone may reduce LER, since the more flexible polymers will be able to easily rearrange [12]. Contrasting this study, Namatsu proved that flexible polymer molecule will become entangled to form aggregates. Rigid polymers are less likely to go through transformation of forming aggregates. Thus, LER would be lower for the more rigid polymers [19]. As presented here, the effect of polymer resin on LER is evident, though the exact nature of this effect is still not understood.

3.3.1.3 Photo Acid Generator (PAG)

According to previously conducted research, the effect of each component in the photoresist and their potential affect on LER is unquestionably evident. There have been

extensive studies to understand the role of PAG molecules in LER formation. One such study indicates that size of the acid molecule produced during the acid-catalyzed reaction contributes to LER formation. The scientists rationalize their observations by indicating that reducing the size of acid molecules will increase the acid diffusion through polymer, therefore reducing the strong polymer and PAG interactions.

The study was repeated by increasing the size of the acid molecule. The obtained results were in agreement with the previous studies that have confirmed diffusion length was proportional to the size of acid molecule size or PAG concentration [24]. Although the provided results were convincing, the affect of PAG on LER performance varies depending on the system of polymer-PAG formulation and the strength of the chemical interaction between these two, as well as other components in the solution.

3.3.2 Surface Roughness Analysis

In the recent years, atomic force microscopy has become one of the widely used tools in surface topography analysis due to its efficiency and practicality. As a surface characterization tool, AFM has gained popularity in the semiconductor world as defect analysis and characterization tool.

In a study conducted by Kostecki and colleagues, AFM was used to study surface morphology and interface properties of commonly used photoresist materials. Materials considered for this study consisted of two positive resists (AZ-4330 and OIR-897) and a negative resist (XPSU) [18]. The product composition of resists contained variations of ethyl-3-ethoxypropionate, 1-methoxy-2-propanolacetate, Novolac polymer, and

naphthoquinone diazide ester. The samples were applied on silicon substrates deposited with a thin layer of Si_3N_4 which were then heated to 600°C - 1100°C [18].

The resist material consisting of linear carbon chains processed at lower temperatures had uniform surface properties, whereas non-linear carbon chain structured photoresist material processed at higher temperatures had high peak to valley ratios [18].

Kostecki observed variations in the height of the granules based on different ratios of material formulations, as shown in Figure 9. The conclusion indicated that the degree of crosslinking would impact the microstructure and the molecular arrangement of materials on the surface [18].

In the first case, where linear carbon chains were processed at lower temperatures there was not enough energy to increase molecular energy to form three dimensional structures. Thus, surface properties were uniform and degree of crosslinking was low. Whereas in the case of non linear carbon chains that were treated at high temperatures, there was enough energy to promote impulsive and repulsive forces. This physical situation resulted in a three dimensional structures, thus forming large aggregates on the surface of the substrates. The formation of these large aggregates would result in rougher surface properties [18].

Figure 9: AFM Images of Resist Material on Silicon Substrate: a) Linear Molecular Chain, Low Exposure Temperature and b) Nonlinear Molecular Chain , High Exposure Temperature [18].

In another experimental study, AFM analysis was utilized to evaluate surface properties of two chemically amplified positive-tone resists with respect to various process variables. The considered resist materials were for 193 nm and 248 nm technology that contained silicon polymers [25].

As indicated in this study, scientists were able to both visually and statistically prove significant differences in the studied systems. For example, in the generated AFM images, the films contained various ratios of protected and unprotected polymers that ranged from 100% to 0% in weight. The protected and unprotected polymer films of 193 nm resist were then baked at 120°C for 5 minutes. The films with 20% or less unprotection group exhibited a smooth surface, whereas all other blend of films formed domain morphology due to protected and unprotected polymers that formed a clear phase separation [25].

As shown in Figure 10, the AFM analysis of this resist under different process conditions revealed that surface roughness increased with the level of unprotection. As a

result of this study it was concluded that interfacial bond strength of the polymer surface and the PAG strongly depend on configuration of the molecules, roughness of the substrate surface and degree of hydrogen bonding. Furthermore, the study revealed that protected and unprotected polymer chains formed a significant phase separation that lead to surface roughness when the material was processed.

Figure 10: AFM Images of Protected and Unprotected Polymer Blends before and after Development [25].

In a study conducted by Lin and others, the effect of solvent on surface roughness was investigated by AFM analysis. To investigate the solvent effects on surface roughness, solvents with different functional groups and boiling points were utilized. The solvents consisted of various carbonyl, carbonyloxy, or hydroxyl groups. Surface roughness was measured on 1x1 μm samples after the films were coated and backed at 95°C. The scientists observed that the solvents with boiling points above 100°C resulted

in a surface roughness of 0.4 nm, whereas the solvents with boiling point below 100°C resulted in a surface roughness of 1 nm. The results of this study indicated that the solvents used in this study affect the molecular interactions, thus controlling the size and the height of the clusters formed on the surface of the substrate [20].

3.4 Conclusion

Established studies in literature clearly indicate the importance of material characterization. These studies have investigated the thermal, chemical, mechanical and performance properties of i-line and g-line resist materials. Through these studies, it has been proven that there are a number of factors that will affect LER, surface roughness, glass transition temperature, and many other parameters. Although, past studies have been able to shed some light on the complex issues affecting resist material performance, there are significant differences in the provided information.

One possible explanation is that resist material consists of multiple components with complex interactions that vary with the system of material combinations used. Therefore, regardless of the available data, it is critical to further understand the interaction of these components for the desired material combinations. By characterizing the various properties of the resist material, it might be possible to develop a material system that will allow the lithography science to overcome current material related technology limitations.

CHAPTER 4

RESEARCH OBJECTIVE AND SCOPE OF EXPERIMENTAL WORK

As technology evolves, the need for faster and larger capacity integrated circuit devices become more important. The continuing desire to reduce cost, increase CPU performance and reduce device size has resulted in limitations in resolution capability of the lithography process. Realization of these limitations is driving development of new materials. Following this trend, semiconductor industry has evolved from 248 nm resist to 193 nm resist to finally 157 nm technology.

4.1 Research Objective

Substrate and resist interaction is one of the key contributors to achieving a good lithographic process, uniform surface topography, and defect free features. Size, complexity, and interaction of the components will result in different lithographic output. As a result of these interactions, important parameters such as magnitude of LER, surface roughness, material decomposition and glass transition temperature will vary.

The proposed study was designed to characterize the effect of resist components (polymer backbone, photoacid generator (PAG and solvent) on chemical and thermal properties of 157 nm resist material. In order to evaluate the effect of resist components on thermal properties of the resist, decomposition and glass transition temperatures were evaluated. It is expected to see higher decomposition and glass transition temperatures for materials with higher molecular weight or more complex chemical structures. In an effort to characterize the chemical properties of the resists used in this study, LER was evaluated. The magnitude of LER parameter will determine whether any of the evaluated

resists would meet industry standards. Additionally, the effect of resist and substrate interaction on the chemical and thermal properties was evaluated.

4.2 Justification

Material improvements have been an integral part of technology advancement in lithography. In a lithography process, resists with different physical and chemical characteristics impact the lithographic performance. A successful lithography process requires thermally and chemically stable materials.

Recently published studies on 193 nm and 248 nm resists indicate the importance of thermal and analytical material characterization. The existing body of knowledge provides valuable information regarding resist performance; however there is limited data on 157 nm resists. Additionally, the conducted studies were performed using different material formulations, under dissimilar conditions. Alteration of any resist components will change the performance of the material. Generating thermal and analytical data for 157 nm resist material would provide valuable insight on the effect of chemical interaction, temperature and substrate.

CHAPTER 5

EXPERIMENTAL APPROACH

5.1 Overview of Experimental Program

The purpose of this research was to investigate the properties of 157 nm photoresist material used in an advanced lithography process. Table 2 summarizes equipment set used in this experimental work. The thermal properties of 157 nm resist were analyzed by employing two thermalanalytical tools: Modulated Differential Scanning Calorimeter (MDSC), and Thermo-gravimetric Analyzer (TGA). The surface properties were characterized using, Static Contact Angle (SCA), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy.

Table 2: A summary of the equipment Used for this Investigation.

Equipment Type	Parameter	Purpose
AFM	Surface Roughness	Surface property characterization
SCA	Static Contact Angle and Surface Energy	Surface property characterization
MDSC	Tg, Cross-linking	Chemical characterization
SEM	LER	Performance characterization
TGA	Decomposition Temperature	Chemical characterization

As represented in Table 3, a total of 12 experimental conditions were carried out by varying three substrates, and four resist combinations. In these experiments, commercially available wafer substrates consisting of SiON, SiN, and a newly developed

anti reflective coating substrate, SLAM were used. The 200 mm wafers were coated with resist material. The wafers consisted of an $11 \times 11 \text{ mm}^2$ patterned matrix as well as blank regions (Figure 11).

Table 3: Summary of Material and Substrate Combination.

Resist	Solvent	PAG	Polymer	Substrate
R1	Solvent 1 (Methanol)	PAG 1	Polymer 1 (Fluorine based resin)	SiN
R1	Solvent 1 (Methanol)	PAG 1	Polymer 1 (Fluorine based resin)	SiON
R1	Solvent 1 (Methanol)	PAG 1	Polymer 1 (Fluorine based resin)	SLAM
R2	Solvent 2 (2-Heptanone)	PAG 1	Polymer 1 (Fluorine based resin)	SiN
R2	Solvent 2 (2-Heptanone)	PAG 1	Polymer 1 (Fluorine based resin)	SiON
R2	Solvent 2 (2-Heptanone)	PAG 1	Polymer 1 (Fluorine based resin)	SLAM
R3	Solvent 2 (2-Heptanone)	PAG 2	Polymer 1 (Fluorine based resin)	SiN
R3	Solvent 2 (2-Heptanone)	PAG 2	Polymer 1 (Fluorine based resin)	SiON
R3	Solvent 2 (2-Heptanone)	PAG 2	Polymer 1 (Fluorine based resin)	SLAM
R4	Solvent 2 (2-Heptanone)	PAG 2	Polymer 2 (Silicon based resin)	SiN
R4	Solvent 2 (2-Heptanone)	PAG 2	Polymer 2 (Silicon based resin)	SiON
R4	Solvent 2 (2-Heptanone)	PAG 2	Polymer 2 (Silicon based resin)	SLAM

A flow chart summarizing the experimental approach to characterize 157 nm resist material is shown in Figure 12. Step 1 involved preparation and coating of wafers with various resists. This step was completed by the suppliers providing the resist materials for evaluation. Step 2 required analyzing the entire set of wafers for surface property effects by using the static contact analytical tool. After completion of surface contact analysis, the wafers were characterized by AFM and SEM. Finally, TGA and MDSC, which are destructive tests, were performed on all samples. Steps 2 through steps 7 were completed at Intel's Fab Material Organization (FMO), in Santa Clara research labs.

Figure 11: Schematic representation of 157 nm patterned wafer.

Figure 12: A Flowchart Summarizing the Basic Processing, Metrology and Analysis Steps for Characterizing 157 nm Resist Materials.

The experimental runs were performed based on experimental designs listed in Tables 4-6. The first part of this study included comparison of resist 1 (R1), and resist 2 (R2). These two resist materials consisted of the same backbone resin, which is based on fluorinated chemistry and the same undisclosed photo acid generator (PAG) but a different solvent (Methanol vs. 2-Heptanone) (see Table 3). The LER, surface roughness, surface polarity, and thermal stability of these resists were analyzed as a function of resist solvent.

Table 4: Experimental Runs for R1 &R2 to Determine Solvent Effects.

Resist	Substrates			Experimental Matrix				
				CA	AFM	SEM	TGA	MDSC
R1	SiN	SiON	SLAM	16 Data Points	3 runs per wafer	3 features per wafers	1 per wafer	1 per wafer
R2	SiN	SiON	SLAM	16 Data Points	3 runs per wafer	3 features per wafers	1 per wafer	1 per wafer

As shown in Table 5, the second part of the investigation focused on the comparison of resist 2 (R2) and resist 3 (R3). These two materials consisted of the same backbone resins (Fluorinated resin) and solvent but different PAG molecules. Comparing these two resists allowed evaluation of PAG effect on LER, surface roughness, surface polarity, and thermal stability.

Table 5: Experimental Runs for R2 & R3 to Determine Photoacid Generator (PAG) Effects.

Resist	Substrates			Experimental Matrix				
				CA	AFM	SEM	TGA	MDSC
R2	SiN	SiON	SLAM	16 Data Points	3 runs per wafer	3 features per wafers	1 per wafer	1 per wafer
R3	SiN	SiON	SLAM	16 Data Points	3 runs per wafer	3 features per wafers	1 per wafer	1 per wafer

Lastly, experimental runs for resist 3 (R3) and resist 4 (R4) were completed.

These two resist formulations consisted of a different polymer backbone but same solvent and PAG molecules. R3 and R4 were evaluated to determine the effect of LER, surface roughness and polarity, and thermal stability (Table 6).

Table 6: Experimental Runs for R3 & R4 to Determine Polymer Effects.

Resist	Substrates			Experimental Matrix				
				CA	AFM	SEM	TGA	MDSC
R3	SiN	SiON	SLAM	16 Data Points	3 runs per wafer	3 features per wafers	1 per wafer	1 per wafer
R4	SiN	SiON	SLAM	16 Data Points	3 runs per wafer	3 features per wafers	1 per wafer	1 per wafer

5.2.1 Surface Characterization

5.2.1.1 Static Contact Angle Analysis (SCA)

The surface characterization studies were conducted by utilizing static contact angle measuring tool. The systems used included a drop dispenser, drop stage, video camera, frame grabber, and a computer (Figure 13). The samples were tested with water.

The data set collected for this study consisted of individual measurements in the unpatterned region of the wafer. In general, static contact angle (SCA) is a technique used to measure the surface properties of dry coatings to predict wetting as a function of surface properties [20]. To quantify the behavior of liquid on the surface, the angle (θ) formed by the liquid-solid interaction is measured (Figure 14).

In order to determine surface wettability, the value of angle is analyzed. If the angle formed $\theta < 90^\circ$, it indicates that the solid is wet by the liquid. Similarly if the angle formed $\theta > 90^\circ$, it indicates non-wetting, where the limits $\theta = 0$ and $\theta = 180^\circ$ indicates full wetting (hydrophilic) and non-wetting (hydrophobic), respectively [26].

Additionally, contact angle (θ) data can be used to evaluate surface energy. Surface energy is determined from a balance of interfacial tensions due to dissimilar materials. It is characterized by Young's equation where σ_{LV} is the interfacial tension between liquid (L) and vapor (V), σ_{LS} is interfacial tension between liquid (L) and solid (S), σ_{SV} is the interfacial tension between (S) and vapor (V) [26].

$$\sigma_{LV}\cos\theta + \sigma_{LS} = \sigma_{SV} \quad \text{Equation 1}$$

Rearrangement of Equation (1), allows defining surface energy (σ) as follows:

$$\sigma = \sigma_S + \sigma_{LV} - \sigma_{LS} = \sigma_{LV}(1 + \cos\theta) \quad \text{Equation 2}$$

According to studies conducted by Waynes, it has been determined that most polymers can be considered to consist of homologous polymer series, thus it can be assumed that the relationship between the contact angle and wetting tension is linear, allowing to make the assumption that σ_{LV} is fixed at 72 mN/m for water [26]. Using this relationship, contact angle data was used to calculate surface energy due to chemical-substrate interaction.

Figure 13: Contact Angle Tool Setup [26].

Figure 14: A Schematic Illustration of Contact Angle Measurement [26].

5.2.1.2 Atomic Force Microscopy (AFM)

Once the sample evaluation via SCA analysis was completed, atomic force microscopy (AFM) was used to provide physical characteristics of surfaces properties. Each sample was evaluated by applying an AFM scan across an area of a 1x1 μm .

When applying AFM analysis, the most critical component of AFM consists of the tip which is positioned at the end of a cantilever beam. In order to characterize the surface the tip is repelled by or attracted to the surface, and the cantilever beam is deflected. As shown in Figure 15, the magnitude of the deflected beam is captured by a laser. A plot of the deflected laser beam versus the tip position with respect to its position on the sample surface quantifies the variations (hills and valleys) in the surface roughness (RMS). RMS is expressed as

$$RMS = \sqrt{\frac{(h_1)^2 + (h_2)^2 + (h_3)^2 + \dots + (h_n)^2}{n}} \quad \text{Equation 3}$$

where h is the average height or depth [26].

There are two modes that the AFM can work with. One consists of the tip touching the surface (contact mode), and the other is the tip tapping across the surface (tapping mode). In this experimental study the tapping mode was applied to prevent damaging physical properties of the surface.

Figure 15: A schematic of Atomic Force Microscopy [26].

5.2.1.3 Scanning Force Microscopy (SEM)

Line edge roughness analysis was conducted on 100 nm and 40 nm features by using top-down scanning electron microscopy. The analysis was conducted at approximately 200K magnification and 5eV. To reduce charging affects, the wafers were coated with a conductive layer of gold metal.

SEM is based on electron technology (instead of light) to form an image. At the very top of the microscope electrons are produced due to heating of a metallic filament. As shown in Figure 16, the electrons travel a vertical path through electromagnetic lenses. These lenses focus and direct the electrons towards the sample. Once the electrons hit the surface of the sample, some electrons are ejected. The detector collects the backscattered electrons and converts them to a signal which turns into an image [23].

Figure 16: SEM Setup [23].

5.2.2 Thermal Characterization

5.2.2.1 Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) is a method that allows determination of material thermal stability through sample weight changes that occur as a function of temperature and time. As indicated in Figure 17, thermo-gravimetric analysis metrology tool consists of an electronic microbalance, a furnace, a temperature programmer and an output recording instrument [21].

In this study, TGA was used to characterize chemistry decomposition temperature due to dehydration, melting, crosslinking or oxidation of material. Samples weighting

approximately 2-3 mg were exposed to a heat scan at a rate of 5°C/min from room temperature to 250-300°C. The rate of 5°C/min was chosen to minimize thermal lag between the sample and detector.

The TGA thermograms were then analyzed for weight loss variations as a function of temperature. Generally, the mass variation during thermal scan is defined as:

$$\frac{W_f - W_i}{W_i} \times 100\% \quad \text{Equation 4}$$

where W_i is the starting weight, and W_f is the final weight of the material. The temperature of decomposition was assigned as the temperature at which a significant weight change of greater than 5% was observed.

Figure 17: TGA Setup [21].

5.2.2.2 Modulated Differential Scanning Calorimetry (MDSC)

Modulated differential scanning calorimetry tool (Figure 18) was used to further characterize the thermal properties of the resist materials used in this experiment. The measurements provided thermal information associated with thermal transitions in the

materials. Additionally, the MDSC metrology tool was used to measure glass transition temperature (T_g) [21].

In MDSC studies, the sample and an inert reference are exposed to heat in the presence of nitrogen. During the heating process, the sample goes through thermal transitions and these signals are measured. The produced peaks provide information on reversible and irreversible heats of reaction. The rate of reaction is measured by MDSC based on the following equation:

$$\frac{dx}{dt} = C \exp\left(-\frac{E_a}{RT}\right)(1 - X)^n \quad \text{Equation 5}$$

where x is the fraction of the material reacted, t is time, C is the pre-exponential constant, k is the Arrhenius rate constant, n is order of reaction, R is the universal gas constant and E_a is activation energy. In this case, the samples were heated at a rate of $10^\circ\text{C}/\text{min}$. The area under the curve was analyzed to obtain various thermal properties such as reversing endothermic or exothermic heats of reactions. MDSC calculates glass transition temperature based on simple mathematics of integrating area under the curve which provides a direct correlation of weight loss vs. temperature.

The irreversible nature of the endothermic peak was confirmed by using a second, repeated heat of the same sample. Absence of the heat peak during the second heating cycle implies that all irreversible reactions have been completed during the first heat (Appendix D).

Figure 18: MDSC Setup, [21].

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Solvent Effects

6.1.1 Surface Contact Angle Analysis

To determine the effect of solvent on resist wettability properties, static contact angle data for R1 and R2 were evaluated. Table 7 shows contact angle data for resist 1 (R1) and resist 2 (R2) on SiN, SiON, and SLAM substrates, respectively. As represented in Table 7, both R1 and R2 have surface angles (θ) less than 90° , which is an indication of hydrophilic surface properties.

Table 7: Contact Angle (θ) analysis for R1 and R2 on SiN, SiON and SLAM.

Parameter	R1-SiN	R1-SiON	R1-SLAM	R2-SiN	R2-SiON	R2-SLAM
Average Contact Angle (θ)	77.23	77.95	82.93	72.93	74.21	82.40
Standard Deviation	19.26	8.98	13.81	16.55	18.32	15.37

Based on Young's Equation, which was represented in Chapter 5, surface energy values for R1 and R2 were calculated. Table 8 shows the general statistical summary and distribution of surface energy values for R1 and R2. Additionally, Figure 19 demonstrates surface energy outputs for R1 and R2 on all substrates. As represented in Table 8 and Figure 19, R1 and R2 had surface energy values averaging 49-69 mN/m. To further evaluate the data 2-sided t-test and p-values were evaluated. Results from statistical analysis is represented in Appendix A. Statistical analysis indicate that R1 has

significantly higher mean and standard variation values of surface energy (Appendix A-Table 27-29). Furthermore, surface properties of R1 and R2 with respect to substrate were investigated. As represented in Table 8, resist properties are independent of substrate properties.

Figure 19: Surface Energy Analysis for R1 and R2 on SiN, SiON and SLAM.

Table 8: Surface Energy Values for R1 and R2 on SiN, SiOn, and SLAM Substrates.

Level	Mean (mN/m)	Standard Deviation (mN/m)
R1-SLAM	67.09	56.95
R1-SiN	61.19	49.24
R1-SiON	88.03	44.71
R2-SLAM	49.38	55.64
R2-SiN	28.83	29.80
R2-SiON	68.79	58.25

6.1.2 Atomic Force Microscopy Results

AFM analysis was performed to determine effect of solvent on surface roughness. As shown in Table 9, there is a clear correlation between surface roughness and solvents used in this experiment. From the images represented in Figure 20-25, it could be seen that R1 and all substrate combinations have distinctly larger clusters in comparison to R2 with the same substrate combinations. The findings were further confirmed by evaluation of individual size and width of various clusters formed on the surface of these substrates. Table 9 and data represented in Appendix B (Figures 60-65) shows the summary of the data indicating the range of variation in width and height of clusters. Data confirms that R1 has much larger clusters with significantly wider range of variation in size.

Table 9: Summary of Surface Roughness Analysis for R1 and R2.

Substrate	Resist	Roughness (nm)	Average Height of clusters (nm)	Range of Height of clusters (nm)	Average Width of clusters (nm)	Range of Width of clusters (nm)	Visual Characterization
SiN	R1	2.183	26	(17-26)	28	(16-40)	Round & Dense
SiON	R1	1.947	24	(13-47)	10	(7-13)	Round & Dense
SLAM	R1	1.983	26	(21-31)	17	(9-30)	Round & Dense
SiN	R2	0.458	9	(1-15)	4	(1-10)	Round & Scattered
SiON	R2	0.528	12	(7-20)	6	(2-10)	Round & Scattered
SLAM	R2	0.544	10	(3-16)	8	(6-12)	Round & Scattered

Figure 20: Result of AFM Analysis for R1 on SiN Substrate.

Figure 21: Result of AFM Analysis for R2 on SiN Substrate.

Figure 22: Result of AFM Analysis for R1 SiON Substrate.

Figure 23: Result of AFM Analysis for R2 on SiON Substrate.

Figure 24: Result of AFM Analysis for R1 on SLAM Substrate.

Figure 25: Result of AFM Analysis for R2 on SLAM Substrate.

For R1 and R2, surface roughness was independent of substrate effects. As shown in Figure 26, it appears that there were no correlations between surface roughness and substrate for any of the resist and substrate combinations.

Figure 26: Comparison of Average Cluster High for R1 and R2 Contributing to Surface Roughness.

6.1.3 TGA and MDSC Analysis

The decomposition temperature of R1 and R2 was determined using TGA thermographs (see Appendix C). TGA analysis revealed three distinct physical changes in the resist due to heating effects. As illustrated in Figure 27, the first region of the graph shows the temperature change due to solvent evaporation. The second region of the graph corresponds to the temperature range at which the decomposition of the PAG molecules occurs, and the last region indicates the temperature range for unprotection of polymer backbone.

Table 10 shows the summary of the thermal transition profile in all regions for R1 and R2. As confirmed by TGA analysis, the solvent evaporation temperature for R1 and R2 starts at approximately 60°C. Similarly, R1 and R2 showed comparable temperature profile and thermal stability in Region II and Region III at approximately 100°C and 200°C, respectively.

Figure 27: TGA Results for R1 and R2 Showing Material Decomposition Temperature.

Table 10: Decomposition Temperature Analysis for R1 and R2.

Resist	Solvent Evaporation Temperature (°C)	PAG Decomposition Temperature (°C)	Polymer Decomposition Temperature (°C)
R1	65±5	100±3	201±5
R2	60±3	105±3	200±7

MDSC was used to determine glass transition temperature (T_g) of resist materials. In the case of R1 and R2, the glass transition temperatures were similar and ranged from 73.9°C to 74.18°C. Additionally, the MDSC data shows the heat flow for R1 and R2. The data showed that R1 has a larger exothermic heat flow (1728.78 J/g) compared to R2 (1147.73 J/g), which was an indication of irreversible reaction.

6.1.4 Scanning Electron Microscopy Analysis

In order to determine the effect of solvent on line edge roughness top-down SEM analysis on 40 nm and 100 nm feature size was conducted. Tables 11 and 12 present summary of LER. Statistical analysis for 40 nm and 100 nm feature size for R1 and R2 are represented Appendix E. Figures 28 and 30 represent typical SEM output indicating magnified line edge variations. Additionally, Figures 29 and 31 show graphical representation of LER output values for R1 and R2 for 40 nm and 100 nm feature sizes. As represented in Tables 11-12, and Figures 28-31, the average and variation of LER for R2 and R3 were significantly different for all substrate and resist combinations for both feature sizes. Additionally, no impact of substrate on LER was observed.

Table 11: Results of 3σ Line Edge Roughness for R1 and R2 for 100 nm Feature Size.

Level	Mean (nm)	StdDev (nm)
R1-SiN	7.21	0.78
R1-SiON	10.42	1.58
R1-SLAM	9.35	1.30
R2-SiN	6.52	0.55
R2-SiON	6.69	1.44
R2-SLAM	6.04	1.42

Table 12: Results of 3σ Line Edge Roughness for R1 and R2 for 40 nm Feature Size.

Level	Mean (nm)	StdDev (nm)
R1-SiN 2	8.96	0.30
R1-SiON 2	8.61	1.14
R1-SLAM 2	9.81	0.61
R2-SiN 2	7.21	0.66
R2-SiON 2	7.55	0.31
R2-SLAM 2	7.38	0.85

Figure 28: Results of SEM Analysis for 100 nm Features for R1 and R2 on SiN, SiON and SLAM Substrates.

Figure 29: Graphical Results for 100 nm Features Showing Data Variations of LER for R1 and R2.

Figure 30: Results of SEM Analysis for 100 nm Features for R2 and R3 on SiN, SiON and SLAM Substrates.

Figure 31: Graphical Results for 40 nm Features Showing Data Variations of LER for R1 and R2.

6.2 PAG Effect

6.2.1 Contact Angle Analysis

To evaluate the effect of PAG on surface properties, contact angle analysis was conducted for R2 and R3. Table 13 shows a summary of the contact angle data for R2 and R3. As represented in Table 13, R3 values are significantly higher than R2 for all substrates. However, all resist and substrate combinations have mean and variations values which were less than 90°, an indication of hydrophilic surface properties.

Table 13: Contact Angle (θ) analysis for R2 and R3 on SiN, SiON and SLAM.

Parameter	R2-SiN	R2-SiON	R2-SLAM	R3-SiN	R3-SiON	R3-SLAM
Average Contact Angle (θ)	46.81	58.52	48.81	75.88	76.46	74.80
Standard Deviation	1.53	1.03	2.12	1.65	1.90	1.96

Resist properties were further evaluated by calculating surface energy values based Young's equation (equation 2) represented in chapter 5. Figure 35 demonstrates surface energy output for R2 and R3 on all substrates. The general summary and distribution statistics are represented in Table 14 and Figure 32. The data shows both R2 and R3 had surface energy values averaging 49-74 mN/m. It was determined that surface energy values corresponding to R3 was much larger compared to R2 on all substrates. Based on the p and t-test statistics these variations were significant, indicating the direct impact of PAG effect (Appendix A- Table 30-32).

Figure 32: Surface Energy Analysis for R2 and R3 on SiN, SiON, and SLAM.

Table 14: Statistical Analysis of Surface Energy Data for R2 and R3.

Level	Mean (mN/m)	Variation (mN/m)
R2-SLAM	49.38	55.64
R2-SiN	81.83	29.80
R2-SiON	68.79	58.25
R3-SLAM	74.65	49.79
R3-SiN	88.99	52.87
R3-SiON	73.59	55.39

6.2.2 Atomic Force Microscopy Analysis

In the case of R2 and R3, the AFM data evaluation was aimed to determine the effect of PAG molecule on surface roughness of the various substrates and resist combinations. Figure 33-38 represent surface roughness measurements from AFM analysis for R2 and R3. Findings show that RMS values of R2 and R3 are comparable indicating that R2 and R3 have similar surface roughness properties on all substrates. Additionally, as represented in Table 15, and in Appendix B (Figures 63-68) analysis of individual cluster height and width confirms findings that the effect of the PAG molecule is not significant. In addition, as shown in Figure 39, no apparent correlation between surface roughness and substrate properties was found.

Table 15: Summary of Surface Roughness Analysis for R2 and R3.

Substrate	Resist	Roughness (nm)	Average Height of clusters (nm)	Range of Height of clusters (nm)	Average Width of clusters (nm)	Range of Width of clusters (nm)	Visual Characterization
SiN	R2	0.458	9	(1-15)	4	(1-10)	Round & Scattered
SiON	R2	0.528	12	(7-20)	6	(2-10)	Round & Scattered
SLAM	R2	0.544	10	(3-16)	8	(6-12)	Round & Scattered
SiN	R3	0.466	8	(6-12)	9	(5-14)	Round & Scattered
SiON	R3	0.458	6	(2-10)	5	(4-6)	Round & Scattered
SLAM	R3	0.432	9	(10-26)	8	(6-10)	Round & Scattered

Figure 33: Result of AFM Analysis for R2 on SiN Substrate.

Figure 34: Result of AFM Analysis for R3 on SiN Substrate.

Figure 35: Result of AFM Analysis for R2 on SiON Substrate.

Figure 36: Result of AFM Analysis for R3 on SiON Substrate.

Figure 37: Result of AFM Analysis for R2 on SLAM Substrate.

Figure 38: Result of AFM Analysis for R3 on SLAM Substrate.

Figure 39: Comparison of Average Cluster Height for R2 and R3 Contributing to Surface Roughness.

6.2.3 TGA and MDSC

The effect of PAG unprotection reaction on thermal stability of R2, and R3 was studied. Figure 40 and Table 16 represent a summary of the thermal performance of R2 and R3. Based on the data, three distinct regions were observed. In the first region where solvent evaporation takes place, both resists performed similarly. Likewise, in the second region, where PAG decomposition takes place, R2 and R3 showed comparable thermal stability characteristics. For both resists, PAG decomposition seemed to occur between 100°C-125°C. In the last region of the thermograms, both resists showed similar polymer decomposition reaction that started at approximately 200°C.

Figure 40: TGA Results for R2 and R3 Showing Material Decomposition Temperature.

Table 16: Summary of Material Decomposition Temperatures for R2, and R3.

Resist	Solvent Evaporation Temperature (°C)	PAG Decomposition Temperature (°C)	Polymer Decomposition Temperature (°C)
R2	60±4	115±5	200±5
R3	65±4	125±2	198±4

MDSC was used to determine glass transition temperature (T_g) of R2 and R3. In the case of R3 and R2, the glass transition temperatures were similar and ranged from 67.8°C to 74.18°C. MDSC analysis provided heat flow for R3 and R2. The data showed that R3 (1213.87 J/g) had slightly larger exothermic heat compared to R2 (1147.73 J/g), an indication of irreversible reaction taking place.

6.2.4 Scanning Electron Microscopy Analysis

Another critical goal of this experimental work was to determine the effect of PAG molecules on resist performance, specifically on LER formation. This was accomplished by conducting SEM analysis on R2 and R3 on 100 nm and 40 nm feature sizes. Figures 41 and 43 show graphical representation of LER values whereas Tables 17 and 18 present data. Actual SEM pictures are also included in Figure 42. Based on the 2-sided t-test statistics that was applied (Appendix F: Tables 42-44) the data shows insignificant variation between R2 and R3 for 40 nm and 100 nm feature sizes. The average and variation of LER for R2 and R3 were similar for all substrate and resist combinations for both feature sizes. Additionally, no impact of substrate on LER was observed.

Table 17: Results of 3σ Line Edge Roughness and Statistical Analysis for R2 and R3 for 100 nm Feature Size.

Parameter	Mean (nm)	Standard Deviation (nm)
R2-SiN	6.52	0.55
R2-SiON	6.69	1.44
R2-SLAM	6.04	1.42
R3-SiN	7.12	0.89
R3-SiON	6.28	0.71
R3-SLAM	7.14	0.54

Table 18: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 for 40 nm Feature Size.

Parameter	Mean (nm)	StdDev (nm)
R2-SiN 2	7.21	0.66
R2-SiON 2	7.55	0.31
R2-SLAM 2	7.38	0.85
R3-SiN 2	7.48	0.61
R3-SiON 2	7.04	0.74
R3-SLAM 2	6.45	0.79

Figure 41: Graphical Results for 100 nm Features Showing Data Variations of LER for R2 & R3.

Figure 42: Results of SEM Analysis for 100 nm Features for R2 and R3 on SiN, SiON and SLAM Substrates.

Figure 43: Graphical Results for 40 nm Features Showing Data Variations of LER for R2 and R3.

6.3 Polymer Effect

6.3.1 Contact Angle Analysis

To determine the effect of polymer on surface properties, contact angle analysis was performed. Based on the generated data, all resist and substrate combinations have contact angles values less than 90° which implies hydrophilic surface properties and similar wettability characteristics (Table 19).

Table 19: Contact Angle (θ) analysis for R3 and R4 on SiN, SiON and SLAM.

Parameter	R3-SiN	R3-SiON	R3-SLAM	R4-SiN	R4-SiON	R4-SLAM
Average Contact Angle (θ)	76.46	75.88	74.80	79.55	82.46	82.45
Standard Variation	1.90	1.65	1.96	3.19	3.22	3.43

The contact angle data was further evaluated to determine surface energy values for R3 and R4. Figure 44 demonstrates surface energy output for R1 and R2 on all substrates. The general summary and distribution statistics are represented in Table 20 and in Appendix A (Table 33-35). The data shows that both R3 and R4 have similar surface energy values ranging 60-89 mN/m. Based on the 2-sided t-test statistics, all resist and substrate combinations have similar average and standard deviation values. Additionally, data shows that surface polarity or wettability properties of the two resists are independent of the substrate properties.

Figure 44: Surface Energy Analysis for R3 and R4 on SiN, SiON, and SLAM.

Table 20: Statistical Analysis of Surface Energy Data for R3 and R4.

Level	Mean	StdDev
R3-SLAM	74.65	49.79
R3-SiN	88.99	52.87
R3-SiON	63.59	55.39
R4-SLAM	70.52	42.98
R4-SiN	82.59	45.55
R4-SiON	63.92	47.25

6.3.2 Atomic Force Microscopy Analysis

In the case of R3 and R4, surface analysis was performed to evaluate possible impact of polymer backbone on resist surface properties. Figures 45-50 provides visual interpretation of RMS values reported in Table 21. As represented in these figures and figures provided in Appendix B (Figures 66-71), R4 has rougher surface properties in comparison to R3. Comparison of individual cluster height and width showed consistent trend, which indicates higher surface roughness for R4 (Table 21). In addition, as represented in Figure 51, surface roughness for R3 and R4 are independent of the substrate effects.

Table 21: Summary of Surface Roughness Analysis for R3 and R4.

Substrate	Resist	Roughness (nm)	Average Height of clusters (nm)	Range of Height of clusters (nm)	Average Width of clusters (nm)	Range of Width of clusters (nm)	Visual Characterization
SiN	R3	0.466	8	(6-12)	9	(5-14)	Round and Scattered
SiON	R3	0.458	6	(2-10)	5	(4-6)	Round and Scattered
SLAM	R3	0.432	9	(10-26)	8	(6-10)	Round and Scattered
SiN	R4	0.817	10	(8-10)	6	(2-10)	Spiky and Dense
SiON	R4	0.732	10	(7-12)	5	(1-7)	Spiky and Dense
SLAM	R4	0.854	11	(6-10)	6	(2-6)	Spiky and Dense

Figure 45: Result of AFM Analysis for R3 on SiN Substrate.

Figure 46: Result of AFM Analysis for R4 on SiN Substrate.

Figure 47: Result of AFM Analysis for R3 on SiON Substrate.

Figure 48: Result of AFM Analysis for R4 on SiON Substrate.

Figure 49: Result of AFM Analysis for R3 on SLAM Substrate.

Figure 50: Result of AFM Analysis for R4 on SLAM Substrate.

Figure 51: Comparison of Average Cluster High for R3 and R4 Contributing to Surface Roughness.

6.3.3 TGA and MDSC Analysis

The effect of polymer resin on thermal stability of the R3, and R4 was studied. Table 22, represents a summary of the thermal transition regions of R3 and R4. As shown in Figure 52, three distinct regions were observed. In the first region where solvent evaporation takes place, both resists performed similarly. In the second region, where PAG decomposition takes place, R2 and R3 showed comparable thermal stability characteristics. For both resists, PAG decomposition occurred between 100°C-125°C. In the last region of the thermograms the decomposition reaction of the resin for R3 occurs at approximately 198°C whereas in the case of R4 this reaction starts at 140°C.

Figure 52: TGA Results for R3 and R4 Showing Material Decomposition Temperature.

Table 22: Summary of Material Decomposition Temperatures for R3, and R4.

Resist	Solvent Evaporation Temperature (°C)	PAG Decomposition Temperature (°C)	Polymer Decomposition Temperature (°C)
R3	65±5	125±3	198±3
R4	50±6	120±7	140±4

To determine the impact of polymer chain on glass transition temperature, R3 and R4 were exposed to heat cycling process via MDSC analysis. The glass transition temperature for R3 was 67.8°C, whereas the transition temperature for R4 was significantly higher (105 °C). Additionally, the MDSC data shows the heat flow for R3 and R4. The data demonstrates that R4 (5126.67 J/g) has a larger magnitude of exothermic heat flow compared to R3 (1213.87 J/g).

6.3.4 Scanning Electron Microscopy Analysis

Based on this investigation and previous discussions, it has been determined that resin polymer has significant impact on formation of line edge roughness. SEM analysis was performed to confirm and determine the extend of the effect of polymer resin on LER formation.

Tables 23 and 24 and Tables 48-52 in Appendix G represent statistical evaluation of LER formation at 100 nm and 40 nm dimensions. Figure 53 is a typical SEM output used to obtain LER is provided. Figure 54 and 55 represent graphical output of the statistical data shown in Tables 23 and 24 for 100 nm and 40 nm feature size, respectively.

As represented in Figures 54-61 and Tables 23-24, it is apparent that polymer backbone contributes to LER formation. Based on the statistical analysis, the two resists perform differently for both 100 nm and 40 nm feature size. Although the mean for the analysis were significantly different, within sample variation was minimal. Also, from the statistical analysis, it is also evident that the magnitude of the LER increases with

decreasing feature size. Finally, no direct impact of substrate was observed. All resist materials performed indifferently with respect to substrate.

Figure 53: Results of SEM Analysis for R3 and R4 on SiN, SiON and SLAM Substrates.

Figure 54: Graphical Results for 100 nm Features Showing Data Variations of LER for R3 and R4.

Table 23: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 for 100 nm Feature Size.

Level	Mean (nm)	StdDev (nm)
R3-SiN	6.12	0.89
R3-SiON	6.28	0.71
R3-SLAM	7.14	0.54
R4-SiN	8.04	0.67
R4-SiON	10.23	0.51
R4-SLAM	8.92	0.14

Figure 55: Graphical Results for 40 nm Features Showing Data Variations of LER for R3 and R4.

Table 24: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 for 40 nm Feature Size.

Level	Mean (nm)	StdDev (nm)
R3-SiN 2	7.48	0.61
R3-SiON 2	7.04	0.74
R3-SLAM 2	6.45	0.79
R4-SiN 2	9.77	1.29
R4-SiON 2	11.36	1.42
R4-SLAM 2	12.44	3.02

CHAPTER 7

CONCLUSIONS

In the recent years, process complexity of lithography for advanced semiconductor technology has significantly increased. In the complicated lithography technology, substrate properties and its interaction with resist affect material performance. In addition, it has been proven that various chemical components of resist impact the organization of the molecules on the surface of the substrate. The impact of these variations has a profound effect on the lithography process and dimensional quality. Thus, a study was proposed to characterize 157 nm resist by evaluating the effect of (PAG) compound, solvent and platform resin on chemical and thermal properties of 157 nm resist material. Additionally, the effect of resist and substrate interaction was also investigated. The results of this study have shown that these parameters have a significant impact on resist properties.

7.1 Contact Angle and Surface Energy

To evaluate physical characteristics of the resists used in this study contact angle measurements were conducted. The experiment revealed no distinctly different behavior of resist material with respect to solvent, PAG, polymer or substrate effects. In general, the data set corresponding to all resist and substrate combinations had similar mean and variations in the data. All resist and substrate combinations were determined to have hydrophilic surface properties. Further evaluation of surface properties of resists indicates that surface energy is impacted by solvent, PAG, and polymer properties and is independent of substrate effects.

7.2 Surface Roughness

In an effort to provide some insight on the quality of the resist surface texture for the resist films used in this study, surface roughness was measured with AFM.

According to the performed analysis the average surface roughness of the resist was mostly impacted by solvent effects. It appeared that R2, which had a solvent with a boiling point well above 100°C, resulted in smoother surface properties. Whereas R1, which consisted of a solvent with a boiling point less than 100°C, had much rougher surface topography. This observation could be attributed to the fact that the impact of solvent on surface topography was due to high evaporation rate of the low boiling point solvent during coating and baking process. As the solvent evaporates prematurely, it could contribute to rearrangement of the molecules and forming three dimensional structures or clusters that result in rough surfaces.

These results were clearly in agreement and complementary to the previously done research. In his studies, Lin tested the effect of solvent on surface roughness by studying a wide range of solvents with different boiling points [21]. For the particular system of interest, he also observed that solvents with boiling points less than 100°C resulted in a much more significant surface roughness variations compared to solvents with boiling points above 100°C. Lin concluded that solvent in a resist polymer solution determined the conformation of the polymer and consequently their sizes.

In addition to solvent effects, it was also proven that polymer properties influence the surface roughness. As the molecular weight and length of polymer chain increased so did the surface roughness. One could see that the short polymer chains resulted in

smaller clusters whereas polymer structures with long chains resulted in larger clusters. This increased the magnitude of surface roughness. Another possible explanation for this observation was that as the resist was coated and treated with post bake heating cycle, the polymer went through crosslinking process. This process resulted in molecules that formed clusters and the severity of these clusters was directly proportional to length of polymer chains.

This observation complemented the work of Kostecki and others, which showed that resist material consisting of linear carbon chains had homogenous surface properties, whereas photoresist material that consisted of non-linear structure consisted of high peak to valley ratios [18]. Their study concluded that degree of crosslinking would impact the microstructure and the molecular arrangement of materials on the surface. It also indicated that polymers with long molecular chains would form a three dimensional structure, thus resulting in large aggregates on the surface of the substrates. The formation of these large aggregates would result in rougher surface properties.

In contrast to solvent and polymer effects, there was no apparent impact of PAG molecule and substrate on surface roughness. This trend was unexpected since in chemically amplified resists the interaction of insoluble resin and the PAG molecules are responsible for initiating a catalytic reaction. This catalytic reaction results in increased level of molecular rearrangement. Eventually, the molecular rearrangement forces unprotection of the polymer through hydrogen bonding. The increased level of chemical interaction forces molecules to form three dimensional arrangements which result in rougher surfaces. Thus one could conclude that interfacial bond strength of the polymer

surface and the PAG strongly depended on configuration of the molecules, and degree of hydrogen bounding.

The findings from this study are in disagreement with previously reported literature results. Lin and his colleagues studied the effect of PAG molecules on surface roughness by conducting surface roughness analysis [20]. Their findings indicated that the polymer and acid react. As acid diffuses and reacts with blocking groups, it initiates a catalytic reaction which results in unprotection of the blocking groups. It was observed that the stronger the interaction between the blocking groups and the PAG molecules, the rougher the surface properties of the resist and substrate combination.

In contrast, our study indicates that there was no apparent correlation between surface roughness and substrate properties. One possible explanation for this observation is that all substrates were treated with adhesion promoting primer. The interaction of the primer with the substrate possibly diminished the effect of resist interaction with these various substrates. Therefore, no direct impact of substrate was observed.

7.3 Line Edge Roughness

In an effort to develop materials to meet new technology requirements, it is critical to understand the impact of various parameters on overall resist performance. One such parameter is the line edge roughness of the resist patterns. In order to characterize LER of the substrate and resist combinations used in this study, representative top down SEM images of 100 nm and 40 nm features were investigated (Appendix H). Analyzed scans of the images of R1 and R2 indicate that one of the most

significant impacts to line edge roughness is solvent effects. As previously discussed, the effect of solvent evaporation on molecular arrangement has been studied extensively. Previous studies have shown that significant rough edges variations due to solvent evaporation could be observed. As the solvent evaporates, long polymer chains rearrange themselves and form three dimensional aggregates, thus resulting in an increase in LER. The larger the polymer backbone, the more significant and detrimental the effect of solvent becomes.

The second most detrimental effect was due to resin polymer variations. The data of R3 and R4 showed that there is a direct correlation between the length of resin chain and the line edge roughness. As the polymer length increased so did the magnitude of LER. When lengthy polymers are exposed to harsh processing conditions, they go through many reactions. As a result of these reactions, they rearrange themselves and some form clusters. The size of these clusters is much larger in size when the polymer consists of long sequential units. In addition, due to this new orientation, the chemical interactions force the molecules to form a three dimensional structure which results in LER.

One of the primary reasons for the cluster formation could be flexibility or rigidity of resin polymers. Previous studies have shown that flexible molecules result in reduced LER since they form a smooth surface due to easy rearrangement of molecules. Another explanation for this observation could be due to formation of nonlinear molecules caused by attracting chemical forces. Strong chemical attractions will result in increased magnitude of LER formation.

Thirdly, it was observed that although PAG molecules also impacted line edge roughness, the direct impact of PAG molecules was not as severe as in the case of solvent and backbone polymer. This implied that although the PAG molecule might be contributing to LER variations, various PAG molecules have similar effects. The findings from this experiment were in disagreement with previously conducted research [18]. In a chemically amplified resist, the PAG molecule, when exposed to heat, initiates a chemical reaction that produces acid molecules. This reaction produces additional acid molecules that react with protected polymer chains, thus impacting the solubility of the resist.

In a study conducted by Namatsu and others, the size of the acid molecule produced during the acid-catalyzed reaction was investigated. The conclusion from this study indicated that size of acid molecules contributed to LER formation. They rationalized this observations by indicating that reducing the size of acid molecules will increase the acid diffusion through polymer and reduce the strong polymer and PAG interactions [19]. The study was repeated by increasing the size of the acid molecule. The obtained results were in agreement with the previous studies that confirmed diffusion length was proportional to the acid molecule size or PAG concentration. Based on Namatsu's investigation, it is unclear if the lack of correlation in our study in LER is due to PAG effect [19].

In order to determine effect of impact of these components at a smaller technology node, the SEM analysis was repeated on 40 nm features. The data indicated a similar trend with respect to various resist components. However, in addition to

previously observed trends, it could be concluded that LER increases with decreasing feature size. The magnitude of LER for 40 nm was worse for resists R1 and R4. The observed trend consistently proved that effects of solvent and polymer are significant contributors to LER.

Along with line to line variations, the effect of substrate on LER was evaluated. The data showed no obvious correlation of line edge variations with respect to substrate properties. The accuracy of these results could not be confirmed due to limited literature on this subject. Previously conducted researches were based on various surface primers and their impact on adhesion [12]. Since, surface primers were not varied in this experiment, a direct comparison could not be made.

Lastly, generated scans were evaluated based on LER specification established by Advanced Tool Development Facility (ATDF) of International SEMATECH. Most recent benchmarking data established by ATDF required LER value of less than 6% of the width of the line. As represented in Table 25, all resist and substrate combinations failed to meet minimum requirements for LER.

Table 25: LER Data for 100 nm and 40 nm Patterned Features.

Substrate	100 nm					40 nm				
	ATDF Specification (LER<6%)	R1	R2	R3	R4	ATDF Specification (LER<6%)	R1	R2	R3	R4
SiN	6.00	7.07	6.55	7.12	8.04	2.40	9.21	7.30	7.48	9.77
SiON	6.00	7.63	6.68	6.28	10.23	2.40	8.61	7.55	7.04	11.36
SLAM	6.00	8.19	6.04	7.14	8.92	2.40	9.81	7.38	6.12	12.44

In general, although there are numerous research regarding the impact of solvent, PAG and resin on resist properties, there seems to be disagreement as to whether the impact of any one of these components downsize the effect of one another on the overall performance and properties of the resist. Considering that the impact of any one of these components will vary according to the system of materials making up the resist, these observations emphasize on the complexity and the lack of thorough understanding of mechanisms controlling the resist properties.

7.4 Thermal Stability

To determine the thermal stability of the resists evaluated in this study, decomposition and glass transition temperatures were evaluated. Results from the thermoanalytical analysis indicated that R1, R2 and R3 have similar glass transition temperature of approximately 70°C, whereas the glass transition temperature of R4 was 105°C. This finding showed that degree of crosslinking due to polymer structure was significant and could improve thermal stability.

The higher glass transition temperature for R4 was attributed to multiple reasons. One such a rationalization was that plasticization of the polymer matrix by the photo acid generator molecules could result in microphase separation. The phase separation would result in resist materials with various physical and chemical properties. As a result of this phase separation, which might be more dominant in R4, different glass transition temperatures would be obtained.

Additionally, in general the resist material has amorphous properties. The physical properties of resist material are established by molecular movement of individual polymer chains. In the case of R4, the polymer decomposition starts at approximately 140°C and ends at 270°C, whereas in the case of the other resists the polymer decomposition did not take place until the temperature reached 200°C. Findings indicate that the short polymer chains have higher heat resistance properties due to their rigid and tight molecular structures. Whereas in the case of longer polymer chains the heat resistance is not as strong due to their flexible structures. Additionally, it is important to take into consideration the possible role of side chains that might complicate decomposition temperature of resists studied.

In this case since the exact chemical composition of the material studied in this experiment is not disclosed it is difficult to rationalize the specific effect to polymer platform on thermal properties of the resist with a degree of certainty. However, based on our findings it would be rational to assume that increasing molecular weight of the platform polymer will increase steric hindrance. Strong chemical interaction and increased molecular movements due to heat might accelerate material decomposition. Conversely, materials with short polymer chains maintain their rigid structure and will not respond to temperature changes as quickly. This characteristic might result in materials that can stand higher temperatures without significantly changing their properties.

The effect of temperature annealing on material decomposition was also investigated. The solvent evaporation temperature of all resists was similar, hence no

significant impact of solvent on material decomposition temperature was observed. In general, after a resist is spun, substrate is exposed to heating cycle much higher than glass transition temperature. The annealing process results in evaporation of the excess solvent. In this case, these resists and substrate combinations have been exposed to a temperature of 90°C, which had already resulted in evaporation of the most of the solvent in the solution. Thus, the results for R1, R2 and R3 are clearly not enough to conclude affect of solvent on thermal properties of these two resists.

Contrary to solvent effects, PAG molecule decomposition significantly impacted thermal stability of the resist material used in this study. The R2 PAG decomposition occurred at 120°C whereas R3 PAG decomposition occurred at approximately 105°C. Additionally, the transition range for R3 was larger. This observation confirmed the direct impact of PAG molecule on thermal stability of the resist material. The improved thermal stability was due to increased molecular interaction of the PAG molecule and other functional groups.

The findings were also in conflict with previously conducted research. In a study conducted by Liu, the authors looked at resist polymers with and without PAG molecules [21]. The generated data showed that at lower temperatures all synthesized formulations with and without PAG had similar glass transition temperatures. However, at higher temperatures the existence of PAG molecules resulted in increased glass transition temperature. According to Liu, the PAG molecule would increase chemical interactions due to steric hindrance. The increased interaction limited mobility of the polymer chain and therefore resulted in improvements in thermostability of the resist material [21].

As a result of the above explanation, one could assume that the effect of PAG was more dominant in certain concentrations or temperatures. The obtained results could also be attributed to the fact that the existence of other resist components in the solution minimized the effect of the PAG molecule, and thus diminished the direct impact of PAG on thermal stability of the resist.

Lastly, the polymer effects on thermal stability of the resist was evaluated. Findings indicated that the most significant contributor to thermal stability was the polymer backbone. As discussed previously, the average decomposition temperature for R3 was 198°C, whereas in the case of R4, the polymer decomposition started at a lower temperature of 140°C and continued over a large temperature range.

One possible explanation for the variation in resin decomposition is that the interaction between various molecules in the solution is creating more complex isomers of the polymer in the chemical makeup of these resist materials, thus resulting in a higher decomposition temperature of the polymer. Another explanation is that the low decomposition temperature could be attributed to slightly higher molecular weight of the polymer which might have lower heat resistance.

Although it is apparent that each one of the components in resist solution affect the thermal stability of the material at various stages of heat exposure, it is impossible to determine which one of the thermal decomposition stages is most critical or has the most profound effect on the properties of the resist. One reason for this complicated situation is that, in lithography, although processes are setup to achieve the same objective, there is no universal approach to material formulations or the variations of the processing

parameters. Thus, according to the process variables and their predetermined values, the thermal stability of various components of the resist becomes critical.

In addition to glass transition and decomposition effects, the systems of resists were evaluated for heat flow. As summarized in Figure 56, R4 had the larger magnitude of exothermic heat flow compared to all other resists. This could be interpreted as higher resistance to thermal treatment. However, in the first heat cycle, the treatment temperature went well above the decomposition temperature of these resists. Thus, the larger magnitude of heat flow for R1 must be the decomposition energy due to molar unprotected rather than annealing (loss of internal energy).

Figure 56: Summary of Irreversible Heat of Reaction indicating Extend of Reaction.

Throughout the experiment there was a lack of correlation between the effect of substrate and all the parameters that were tested. One possible explanation for this

observation is that the complexity of chemical molecular interaction of various components in the resist is minimizing the substrate effect. Another explanation is that, these systems of resists at the specified concentration of the components are less impacted by the substrate interface.

In conclusion, the purpose of this investigation was fulfilled. The generated data was successful in proving the impact of solvent, PAG, and platform resin on surface energy, surface roughness, glass temperature, decomposition temperature, line edge roughness and substrate. Table 26 summarizes the overall impact of each one of the components studied in this experiment and their profound effect on material properties and performance. Additionally, it was determined that the although the resin polymer effects are significantly more dominant than solvent or PAG molecule effects, the various systems of substrate and resist combinations perform similarly.

Table 26: A Summary of Impact of PAG, Solvent, Polymer on Resist Performance.

Solvent	Hydrophilic	Strong	Higher BP better Lower BP worse	Strong	Weak	Weak
PAG	Hydrophilic	Strong	Independent	Independent	Weak	Weak
Polymer	Hydrophilic	Weak	Smaller MW better Larger MW worse	Strong	Strong	Strong
Substrate	Independent	Independent	Independent	Independent	NA	NA

CHAPTER 8

RECOMMENDATIONS FOR FUTURE WORK

As the process complexity of lithography for advanced semiconductor technology continues to increase, research and development of new material for this application will remain an integral part of technology development activities. As proven by this work, there are many variables that could impact the resist performance.

In order to fulfill the requirements of this study, the scope of this work was based on analysis of solvent, PAG, backbone resin and substrate effects. However, there are many other factors that could be investigated in characterization of materials. In order to improve the understanding of advanced lithography materials and to expand on the results of this investigation, it is recommended to further explore temperature effects.

For example, to truly understand the temperature range for solvent evaporation, PAG, and polymer decomposition one must study resist material that has not been exposed to post bake treatment. Also, it is recommended to analyze resist material that is exposed to a wide range of temperatures. Such analysis would allow for a greater understanding of the primary and secondary temperature effects.

Additionally, analyzing resist material pre and post bake exposure would allow one to determine the level of unprotection. Evaluation of the resist with these characteristics will make it possible to determine the effects of various solvents, PAG molecules and platform resins on unprotection reaction. Further, one could conclude thermal properties of the resist system to achieve a stable microstructure with

homogenous properties, as a result of which the temperature range for various baking processes could be altered.

As a result of this study it has been proven that resin characteristics have profound effects on resist properties. In this study, two polymers were analyzed. One possible improvement to the above findings could be utilization of a resist formulation with the same polymer, but a wider range of molecular weights and chain length polymers. This kind of analysis might help explain the dependency of the resist properties on the molecular structure of the platform resin.

With respect to improving on limitations of this study, there are several additional tests that could be conducted. The concentration of this study was to understand the effect of individual components on material properties and material performance with respect to LER. However, the study did not focus on the effect of inter molecular interactions. For example, instead of varying one variable at a time, it might be worthwhile to conduct experiments by varying two parameters (such as solvent and PAG or PAG and polymer). By doing so, one could determine how the interaction of these components will affect resist performance.

Advancing the investigation of solvent effect on resist performance would provide further insight on the interrelationship of texture and surface roughness. The solvents used in this study had similar boiling points. Although the apparent effect of solvent was distinguishable, experimenting with other solvents would allow one to determine the extent and severity of this phenomena. The interaction of the resist components are rather complex and it is impossible to have a collective description of the intermolecular

reactions that these components participate in. Thus, evaluating the effect of solvent at extreme conditions would allow better understanding of resist properties.

With respect to the effect of resist properties on line edge roughness, it is recommended to further analyze and confirm findings through application of micro-textural analysis. In this investigation, SEM was employed to conduct analysis of LER. When evaluating polymers, this technique has many limitations. One such limitation is the charging effects. Since the resist material is not conductive, in order to prevent charging, low current densities must be utilized. At low current density, resolution is diminished. So, it is recommended to employ a different surface analysis tool. One possible technique is surface roughness measurements on the edges of the isolated and dense lines via AFM. The results of such a study could be compared to the findings of SEM analysis from this study and determine any error that might have been contributed to findings as a result of SEM limitations.

Furthermore, it is recommended to investigate lines with various dimensions. In this study, the analysis was conducted on 100 nm and 40 nm lines. Evaluating the line edge roughness of various dimensions and pitches will help in providing some additional understanding of the effect of solvent, resin and PAG molecule at smaller features.

Additionally, during the development phase of resist technology, 157 nm resist was engineered with the expectation that the new chemistry would improve on limitations of 248 nm and 193 nm resists material. However, as illustrated with representative data for 100 nm and 40 nm features in Figures 57-59, the 157 nm resist technology not only fails to meet industry standards for line edge variations, but also suffers from severe case

of sloped side walls and possibly collapsing. Thus, it is recommended to further investigate capability and limitations of 157 nm resist with respect to these detrimental defects.

Figure 57: Cross Sectional Analysis of 100 nm and 40 nm Patterned Features.

Figure 58: Cross Sectional Analysis of 100 nm and 40 nm Patterned Features

Figure 59: Cross Sectional Analysis of 100 nm and 40 nm Patterned Feature.

Lastly, it is accurate to state that in recent years, process complexity and cost of technology development have significantly increased. Technology and commercial incentives have driven the industry to heavily depend on simulation of processes as an initial step in technology development. In the complicated lithography technology, aerial image modeling has been an ongoing practice. However, resist modeling has been very limited due to the need for confirmation of resist simulated behavior with chemistry data for the specific technology and processes. Recent advancements in this area have made it possible for material suppliers to apply modeling to resist materials. Thus, characterization of the resist performance with modeling simulation would be instructive.

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APPENDIX A
Statistical Analysis of Surface Energy

STATISTICAL ANALYSIS ON SOLVENT COMPONENT OF RESIST (R1 & R2)

Table 27: Statistical Analysis of Surface Energy Data for R1 and R2 on SiN Substrate.

Parameter	R1-SiN	R2-SiN	Test	Test Stat	P-Value	Decision
Mean (mN/m)	61.19	68.83	2-sided t-test	0.04	0.02	P-value > alpha = 0.05. REJECT the hypothesis that Surface Energy R2-SiN Mean = Surface Energy R1-SiN Mean
Variability (mN/m)	49.24	29.80	2-sided F-test	2.73	0.05	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that Surface Energy R2-SiN StdDev = Surface Energy R1-SiN StdDev

Table 28: Statistical Analysis of Surface Energy Data for R1 and R2 on SiON Substrate.

Parameter	R1-SiON	R2-SiON	Test	Test Stat	P-Value	Decision
Mean (mN/m)	88.03	68.79	2-sided t-test	0.46	0.65	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that Surface Energy R2-SiON Mean = Surface Energy R1-SiON Mean
Variability (mN/m)	44.71	58.25	2-sided F-test	1.87	0.21	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that Surface Energy R2-SiON StdDev = Surface Energy R1-SiON StdDev

Table 29: Statistical Analysis of Surface Energy Data for R1 and R2 on SLAM Substrate.

Parameter	R1-SLAM	R2-SLAM	Test	Test Stat	P-Value	Decision
Mean (mN/m)	67.09	49.38	2-sided t-test	0.08	0.9378	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that Surface Energy R2-SLAM Mean = Surface Energy R1-SLAM Mean
Variability (nm)	56.95	55.64	2-sided F-test	1.66	0.3043	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that Surface Energy R2-SLAM StdDev = Surface Energy R1-SLAM StdDev

STATISTICAL ANALYSIS ON SOLVENT COMPONENT OF RESIST (R2 & R3)

Table 30: Statistical Analysis of Surface Energy for R2 and R3 on SiN.

Parameter	R2-SiN	R3-SiN	Test	Test Stat	P-Value	Decision
Mean (mN/m)	81.83	88.99	2-sided t-test	2.21	0.06	P-value < alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiN Mean = R2-SiN Mean
Variability (mN/m)	49.89	52.87	2-sided F-test	4.15	0.0621	P-value < alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiN StdDev = R2-SiN StdDev

Table 31: Statistical Analysis of Surface Energy for R2 and R3 on SiON.

Parameter	R2-SiON	R3-SiON	Test	Test Stat	P-Value	Decision
Mean (mN/m)	68.79	73.59	2-sided t-test	0.25	0.80	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON Mean = R2-SiON Mean
Variability (mN/m)	58.25	55.39	2-sided F-test	1.11	0.84	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON StdDev = R2-SiON StdDev

Table 32: Statistical Analysis of Surface Energy for R2 and R3 SLAM.

Parameter	R2-SLAM	R3-SLAM	Test	Test Stat	P-Value	Decision
Mean (mN/m)	49.38	74.65	2-sided t-test	1.44	0.16	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM Mean = R2-SLAM Mean
Variability (mN/m)	55.64	49.79	2-sided F-test	1.25	0.65	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM StdDev = R2-SLAM StdDev

STATISTICAL ANALYSIS ON SOLVENT COMPONENT OF RESIST (R3 & R4)

Table 33: Statistical Analysis of Surface Energy on SiN for R3 and R4.

Parameter	R3-SiN	R4-SiN	Test	Test Stat	P-Value	Decision
Mean	76.46	79.55	2-sided t-test	3.43	0.02	P-value < alpha = 0.05. DO NOT REJECT the hypothesis that R4-SiN Mean = R3-SiN Mean
Variability(StdDev)	1.90	3.19	2-sided F-test	2.83	0.45	P-value < alpha = 0.05. DO NOT REJECT the hypothesis that R4-SiN StdDev = R3-SiN StdDev

Table 34: Statistical Analysis of Surface Energy on SiON for R3 and R4.

Parameter	R4-SiON	R3-SiON	Test	Test Stat	P-Value	Decision
Mean	73.92	73.59	2-sided t-test	0.56	0.58	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON Mean = R4-SiON Mean
Variability (StdDev)	47.25	55.39	2-sided F-test	1.37	0.52	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON StdDev = R4-SiON StdDev

Table 35: Statistical Analysis of Surface Energy on SLAM for R3 and R4.

Parameter	R3-SLAM	R4-SLAM	Test	Test Stat	P-Value	Decision
Mean	64.65	60.52	2-sided t-test	0.91	0.37	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SLAM Mean = R3-SLAM Mean
Variability(StdDev)	49.79	42.98	2-sided F-test	1.34	0.55	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SLAM StdDev = R3-SLAM StdDev

APPENDIX B
AFM and Comparison of Individual Cluster Height and Width

Figure 60: AFM and Graphical Representation of Individual Cluster Height and Width for R1 on SiN Substrate.

Figure 61: AFM and Graphical Representation of Individual Cluster Height and Width for R1 on SiON Substrate.

Figure 62: AFM and Graphical Representation of Individual Cluster Height and Width for R1 on SLAM Substrate.

Figure 63: AFM and Graphical Representation of Individual Cluster Height and Width for R2 on SiN Substrate.

Figure 64: AFM and Graphical Representation of Individual Cluster Height and Width for R2 on SiON Substrate.

Figure 65: AFM and Graphical Representation of Individual Cluster Height and Width for R2 on SLAM Substrate.

Figure 66: AFM and Graphical Representation of Individual Cluster Height and Width for R3 on SiN Substrate.

Figure 67: AFM and Graphical Representation of Individual Cluster Height and Width for R3 on SiON Substrate.

Figure 68: AFM and Graphical Representation of Individual Cluster Height and Width for R3 on SLAM Substrate.

Figure 69: AFM and Graphical Representation of Individual Cluster Height and Width for R4 on SiN Substrate.

Figure 70: AFM and Graphical Representation of Individual Cluster Height and Width for R4 on SiON Substrate.

Figure 71: AFM and Graphical Representation of Individual Cluster Height and Width for R4 on SLAM Substrate.

APPENDIX C
Thermo-Gravimetric Analysis

Figure 72: Thermo-Gravimetric Analysis of Glass Transition Temperature for R1.

Figure 73: Thermo-Gravimetric Analysis for Non-Reversible Heat Flow for R1.

Figure 74: Thermo-Gravimetric Analysis of Glass Transition Temperature For R2.

Figure 75: Thermo-Gravimetric Analysis for Non-Reversible Heat Flow for R2.

Figure 76: Thermo-Gravimetric Analysis of Glass Transition Temperature For R3.

Figure 77: Thermo-Gravimetric Analysis for Non-Reversible Heat Flow for R3.

Figure 78: Thermo-Gravimetric Analysis of Glass Transition Temperature For R4.

Figure 79: Thermo-Gravimetric Analysis for Non-Reversible Heat Flow for R4.

APPENDIX D
Modulated Differential Scanning Calorimetry Evaluation

Figure 80: Cycle 1 of Modulated Differential Scanning Calorimetry Evaluation for R1.

Figure 81: Cycle 2 of Modulated Differential Scanning Calorimetry Evaluation for R1.

Figure 82: Cycle 1 of Modulated Differential Scanning Calorimetry Evaluation for R2.

Figure 83: Cycle 2 of Modulated Differential Scanning Calorimetry Evaluation for R2.

Figure 84: Cycle 1 of Modulated Differential Scanning Calorimetry Evaluation for R3.

Figure 85: Cycle 2 of Modulated Differential Scanning Calorimetry Evaluation for R3.

Figure 86: Cycle 1 of Modulated Differential Scanning Calorimetry Evaluation for R4.

Figure 87: Cycle 2 of Modulated Differential Scanning Calorimetry Evaluation for R4.

APPENDIX E
Results of LER Statistical Analysis for R1 & R2 for
100 nm & 40 nm Feature Size on All Substrates

Table 36: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SiN Substrate for 100 nm Feature Size.

Parameter	R1-SiN	R2-SiN	Test	Test Stat	P-Value	Decision
Mean (nm)	7.21	6.52	2-sided t-test	1.25	0.028	P-value > alpha = 0.05. REJECT the hypothesis that R2-SiN Mean = R1-SiN Mean
Variability (nm)	0.78	0.55	2-sided F-test	2.05	0.66	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R2-SiN StdDev = R1-SiN StdDev

Table 37: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SiON Substrate for 100 nm Feature Size.

Parameter	R1-SiON	R2-SiON	Test	Test Stat	P-Value	Decision
Mean (nm)	10.42	6.69	2-sided t-test	-3.02	0.04	P-value < alpha = 0.05. REJECT the hypothesis that R2-SiON Mean = R1-SiON Mean
Variability (nm)	1.58	1.44	2-sided F-test	1.21	0.91	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R2-SiON StdDev = R1-SiON StdDev

Table 38: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SLAM Substrate for 100 nm Feature Size.

Parameter	R1-SLAM	R2-SLAM	Test	Test Stat	P-Value	Decision
Mean (nm)	9.35	6.04	2-sided t-test	-2.97	0.04	P-value < alpha = 0.05. REJECT the hypothesis that R2-SLAM Mean = R1-SLAM Mean
Variability (nm)	1.30	1.42	2-sided F-test	1.18	0.92	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R2-SLAM StdDev = R1-SLAM StdDev

Table 39: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SiN Substrate for 40 nm Feature Size.

Parameter	R1-SiN 2	R2-SiN 2	Test	Test Stat	P-Value	Decision
Mean (nm)	8.96	7.21	2-sided t-test	4.16	0.1	P-value < alpha = 0.05. REJECT the hypothesis that R2-SiN 2 Mean = R1-SiN 2 Mean
Variability (nm)	0.30	0.66	2-sided F-test	5.01	0.33	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R2-SiN 2 StdDev = R1-SiN 2 StdDev

Table 40: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SiON Substrate for 40 nm Feature Size.

Parameter	R2-SiON 2	R1-SiON 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.55	8.61	2-sided t-test	1.57	0.019	P-value > alpha = 0.05. REJECT the hypothesis that R1-SiON 2 Mean = R2-SiON 2 Mean
Variability (nm)	0.31	1.14	2-sided F-test	13.60	0.14	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R1-SiON 2 StdDev = R2-SiON 2 StdDev

Table 41: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SLAM Substrate on 40 nm Feature Size.

Parameter	R1-SLAM 2	R2-SLAM 2	Test	Test Stat	P-Value	Decision
Mean (nm)	9.81	7.38	2-sided t-test	-4.04	0.02	P-value < alpha = 0.05. REJECT the hypothesis that R2-SLAM 2 Mean = R1-SLAM 2 Mean
Variability (nm)	0.61	0.85	2-sided F-test	1.96	0.68	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R2-SLAM 2 StdDev = R1-SLAM 2 StdDev

APPENDIX F
Results of LER Statistical Analysis for R2 & R3 for
100 nm & 40 nm Feature Size on All Substrates

Table 42: Results of 3σ Line Edge Roughness and Statistical Analysis for R2 and R3 on SiN for 100 nm Feature Size.

Parameter	R2-SiN	R3-SiN	Test	Test Stat	P-Value	Decision
Mean (nm)	6.52	7.12	2-sided t-test	0.99	0.38	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiN Mean = R2-SiN Mean
Variability (nm)	0.55	0.89	2-sided F-test	2.61	0.55	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiN StdDev = R2-SiN StdDev

Table 43: Results of 3σ Line Edge Roughness and Statistical Analysis for R2 and R3 on SiON for 100 nm Feature Size.

Parameter	R2-SiON	R3-SiON	Test	Test Stat	P-Value	Decision
Mean (nm)	6.69	6.28	2-sided t-test	-0.44	0.68	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON Mean = R2-SiON Mean
Variability (nm)	1.44	0.71	2-sided F-test	4.09	0.39	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON StdDev = R2-SiON StdDev

Table 44: Results of 3σ Line Edge Roughness and Statistical Analysis for R2 and R3 on SLAM for 100 nm Feature Size.

Parameter	R2-SLAM	R3-SLAM	Test	Test Stat	P-Value	Decision
Mean (nm)	6.04	7.14	2-sided t-test	1.25	0.28	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM Mean = R2-SLAM Mean
Variability (nm)	1.42	0.54	2-sided F-test	6.93	0.25	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM StdDev = R2-SLAM StdDev

Table 45: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SiN for 40 nm Feature Size.

Parameter	R2-SiN 2	R3-SiN 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.21	7.48	2-sided t-test	0.51	0.64	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiN 2 Mean = R2-SiN 2 Mean
Variability (nm)	0.66	0.61	2-sided F-test	1.18	0.92	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiN 2 StdDev = R2-SiN 2 StdDev

Table 46: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SiON for 40 nm Feature Size.

Parameter	R2-SiON 2	R3-SiON 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.55	7.04	2-sided t-test	-1.10	0.33	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON 2 Mean = R2-SiON 2 Mean
Variability (nm)	0.31	0.74	2-sided F-test	5.71	0.30	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SiON 2 StdDev = R2-SiON 2 StdDev

Table 47: Results of 3σ Line Edge Roughness and Statistical Analysis for R1 and R2 on SLAM for 40 nm Feature Size.

Parameter	R2-SLAM 2	R3-SLAM 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.38	6.45	2-sided t-test	-1.38	0.24	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM 2 Mean = R2-SLAM 2 Mean
Variability (nm)	0.85	0.79	2-sided F-test	1.15	0.93	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM 2 StdDev = R2-SLAM 2 StdDev

APPENDIX G
Results of LER Statistical Analysis for R3 & R4 for
100 nm & 40 nm Feature Size on All Substrates

Table 48: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 on SiON for 100 nm Feature Size.

Parameter	R3-SiON	R4-SiON	Test	Test Stat	P-Value	Decision
Mean	6.28	10.23	2-sided t-test	7.79	0.00	P-value < alpha = 0.05. REJECT the hypothesis that R4-SiON Mean = R3-SiON Mean
Variability (StdDev)	0.71	0.51	2-sided F-test	1.92	0.69	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SiON StdDev = R3-SiON StdDev

Table 49: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 on SLAM for 100 nm Feature Size.

Parameter	R3-SLAM	R4-SLAM	Test	Test Stat	P-Value	Decision
Mean	7.14	8.92	2-sided t-test	5.55	0.01	P-value < alpha = 0.05. REJECT the hypothesis that R4-SLAM Mean = R3-SLAM Mean
Variability (StdDev)	0.54	0.14	2-sided F-test	15.59	0.12	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SLAM StdDev = R3-SLAM StdDev

Table 50: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 for on SiN 40 nm Feature Size.

Parameter	R3-SiN 2	R4-SiN 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.48	9.77	2-sided t-test	2.78	0.05	P-value < alpha = 0.05. REJECT the hypothesis that R4-SiN 2 Mean = R3-SiN 2 Mean
Variability (nm)	0.61	1.29	2-sided F-test	4.49	0.36	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SiN 2 StdDev = R3-SiN 2 StdDev

Table 51: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 on SiON for 40 nm Feature Size.

Parameter	R3-SiON 2	R4-SiON 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.04	11.36	2-sided t-test	4.68	0.01	P-value < alpha = 0.05. REJECT the hypothesis that R4-SiON 2 Mean = R3-SiON 2 Mean
Variability (nm)	0.74	1.42	2-sided F-test	3.70	0.43	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SiON 2 StdDev = R3-SiON 2 StdDev

Table 52: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 on SLAM for 40 nm Feature Size.

Parameter	R4-SLAM 2	R3-SLAM 2	Test	Test Stat	P-Value	Decision
Mean (nm)	12.44	6.45	2-sided t-test	-3.33	0.03	P-value < alpha = 0.05. REJECT the hypothesis that R3-SLAM 2 Mean = R4-SLAM 2 Mean
Variability (nm)	3.02	0.79	2-sided F-test	14.52	0.13	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R3-SLAM 2 StdDev = R4-SLAM 2 StdDev

Table 53: Results of 3σ Line Edge Roughness and Statistical Analysis for R3 and R4 on SLAM for 40 nm Feature Size.

Parameter	R3-SiN 2	R4-SiN 2	Test	Test Stat	P-Value	Decision
Mean (nm)	7.48	9.77	2-sided t-test	2.78	0.05	P-value < alpha = 0.05. REJECT the hypothesis that R4-SiN 2 Mean = R3-SiN 2 Mean
Variability (nm)	0.61	1.29	2-sided F-test	4.49	0.36	P-value > alpha = 0.05. DO NOT REJECT the hypothesis that R4-SiN 2 StdDev = R3-SiN 2 StdDev

APPENDIX H
Top-Down & Cross Section SEM Analysis for R1 and
Substrate Combinations

Figure 88: Top Down and Cross Sectional Analysis for R1-SLAM For 40 nm Features.

Figure 89: Top Down and Cross Sectional Analysis for R1-SLAM for 100nm Features.

Figure 90: Top Down and Cross Sectional Analysis for R1-SiN For 40 nm Features.

Figure 91: Top Down and Cross Sectional Analysis for R1-SiN for 100nm Features.

Figure 92: Top Down and Cross Sectional Analysis for R1-SiON for 40 nm Features.

Figure 93: Top Down and Cross Sectional Analysis for R1-SiON for 100nm Features.

APPENDIX I
Top-Down & Cross Section SEM Analysis for R2 and
Substrate Combinations

Figure 94: Top Down and Cross Sectional Analysis for R2-SLAM for 40 nm Features.

Figure 95: Top Down and Cross Sectional Analysis for R2-SLAM for 100nm Features.

Figure 96: Top Down and Cross Sectional Analysis for R2-SiN for 40 nm Features.

Figure 97: Top Down and Cross Sectional Analysis for R2-SiN for 100nm Features.

Figure 98: Top Down and Cross Sectional Analysis for R2-SiON for 40 nm Features.

Figure 99: Top Down and Cross Sectional Analysis for R2-SiON for 40 nm Features.

APPENDIX J
Top-Down & Cross Section SEM Analysis for R3 and
Substrate Combinations

Figure 100: Top Down and Cross Sectional Analysis for R3-SLAM for 40 nm Features.

Figure 101: Top Down and Cross Sectional Analysis for R3-SLAM for 100nm Features.

Figure 102: Top Down and Cross Sectional Analysis for R3-SiN for 40 nm Features.

Figure 103: Top Down and Cross Sectional Analysis for R3-SiN for 100nm Features.

Figure 104: Top Down and Cross Sectional Analysis for R3-SiON for 40 nm Features.

Figure 105: Top Down and Cross Sectional Analysis for R3-SiON for 100 nm Features.

APPENDIX K
Top-Down & Cross Section SEM Analysis for R4 and
Substrate Combinations

Figure 106: Top Down and Cross Sectional Analysis for R4-SLAM for 40 nm Feature.

Figure 107: Top Down and Cross Sectional Analysis for R4-SLAM for 100nm Features.

Figure 108: Top Down and Cross Sectional Analysis for R4-SiN For 40 nm Features.

Figure 109: Top Down and Cross Sectional Analysis for R4-SiN for 100nm Features.

Figure 110: Top Down and Cross Sectional Analysis for R4-SiON for 40 nm Features.

Figure 111: Top Down and Cross Sectional Analysis for R4-SiON for 100nm Features.