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# X-RAY DIFFRACTION MEASUREMENTS OF LITHOGRAPHICALLY DEFINED NANOSTRUCTURES

A Dissertation

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering

University of Houston

In Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in Chemical Engineering

> by Ginusha Perera

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# X-RAY DIFFRACTION MEASUREMENTS OF LITHOGRAPHICALLY DEFINED NANOSTRUCTURES

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#### Abstract

The most sophisticated integrated circuits, such as memory chips and microprocessors, are patterned with projection lithography. The performance of semiconductor electronics is coupled to the resolution of the lithographic process. Next-generation nanopatterning requires imaging processes that can achieve sub-20 nm resolution in ultrathin films. Current manufacturing practices are based on projection lithography with chemically-amplified (CA) resists; however, such "top-down" lithographic processes are approaching their intrinsic resolution limits, so alternative techniques like "bottom-up" block copolymer (BCP) self-assembly are increasingly attractive. The physicochemical parameters that control imaging in top-down and bottom-up lithography are very different, but improving either technique requires accurate feedback for the structure of the "latent chemical image." The objectives of this work are to acquire feedback for image formation using advanced X-ray diffraction techniques, and use this data to construct lithography models that include interfacial interactions.

Image formation in CA resists is governed by a coupled reaction-diffusion mechanism. The bulk deprotection kinetics of a glassy poly(hydroxystyrene-cotertbutylacrylate) resin was examined with infrared spectroscopy and stochastic simulations. Experimental data were interpreted with a model based on non-Fickian catalyst transport (subdiffusive behavior), providing strong evidence that reaction front propagation is controlled by polymer dynamics.

Thin films were nanopatterned with electron beam lithography, and the depth dependent shape of the reaction front was measured with variable-incident-angle small-angle X-ray scattering. The image resolution varies with distance from the free surface and substrate interface, where a broader reaction front is detected at the film surface. This behavior is consistent with a surface excess of catalyst, depth dependent polymer dynamics, or both of these factors. Image formation in BCP self-assembly is controlled by thermodynamics. Thin films of a lamellar poly(styrene-b-methyl methacrylate) copolymer were cast on chemo-epitaxial templates, and their depth dependent structure was measured with variable-incident-angle small-angle X-ray scattering. The shape is significantly deformed near the substrate interface. Simulations based on self-consistent field theory suggest that these deformations are associated with copolymer penetration into the underlying template. This data demonstrates that controlling the structure of the copolymer-template interface is critical for implementation of bottom-up lithography.

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#### Chapter 1 Introduction

Miniaturization of feature sizes drives the rapid innovation cycles that lead to improved performance and lower cost [1,2]. As feature size becomes smaller, technology of fabrication needs to be modified to meet industry requirements. At present, projection lithography has become the key fabrication technique with a minimum feature size of 22 nm and below in ultrathin polymeric films. However such topdown lithographic techniques are approaching their intrinsic resolution limits and alternative bottom-up techniques such as block copolymer directed-self assembly are becoming increasingly attractive. The key requirement in image formation techniques is the precise control over feature size and shape with minimal roughness. Therefore, nanomaterials characterization techniques play an important role in understanding the physical and chemical variables that control the image formation in polymeric thin films. In this context, we focus on measuring the depth dependent image resolution in two model systems, chemically-amplified polymers (top-down) and self-assembling block copolymers (bottom-up).

#### 1.1 Top-down Lithography

Lithographic imaging is used to generate circuit patterns on the substrates which are mainly single crystal silicon. Lithographic materials are radiation sensitive polymers called resists. The lithographic process is illustrated in Figure 1.1.



Figure 1.1: Lithographic patterning process.

The resist films are exposed to ultraviolet or x-ray radiation through a mask, or a radiation pattern directly written with a finely focused electron beam. Radiation will alter the resist's chemistry in the exposed regions. Three dimensional relief images are generated on the above film by dissolving in a developer solvent. Depending on the chemistry of resist and developer, the process can be categorized into positive or negative tone: in positive tone imaging, the exposure results in the resist film being more soluble in the developer, while in negative tone imaging the exposure makes the film less soluble [1].

Rayleigh's equation describes the link between lithographic resolution (R), exposing wavelength ( $\lambda$ ) and the size of the numerical aperture (NA) as, R = k<sub>1</sub> $\lambda$ /NA, [1]. Thus, higher resolution can be achieved by reducing the wavelength or increasing the numerical aperture. Wavelength reduction is considered to be the dominant approach to scaling reduction. A key challenge in material characteristics is the transparency to reduced exposure wavelengths. Each of the new technologies demands a new resist system which accommodates the radiation and exposure tool characteristics.

As the minimum feature size continues to shrink, the resist requirements are becoming more and more stringent. The polymeric resin, which is the largest component in the photoresist film after solvent evaporation contributes to all resist characteristics and performance. Two important characteristics are the sensitivity and the contrast [1,3]. As a solution to sensitivity enhancement, the concept of chemical amplification was introduced in early 1980s where a catalytic species generated by irradiation induces a series of subsequent chemical transformations improving the sensitivity by providing a gain mechanism [2]. The chemical amplification concept was proposed by Ito, Willson and Fréchet in 1982. Chemically amplified (CA) resist system has two core components: a polymer resin matrix and a photoacid generator (PAG). Irradiation of PAG produces active species that catalyze a series of chemical reactions. These chemical transformations are generally accomplished in the presence of heat. Therefore, it is a reaction-diffusion mechanism that governs the imaging mechanism, where long catalytic chain "amplifies" the effect of the incident radiation. The heat supplied to the system increases the mobility of the polymer resin matrix, generating free volume in the system enabling the photoacid diffusion and also providing the activation energy for the cleavage reaction.

CA resists are very sensitive, thus requiring low doses for patterning. Sensitivity increases with catalytic chain length, but excessive would result in resolution blur. Photoacid is generated only in the exposed areas (Figure 1.2) resulting in a steep concentration gradient at the interface between the exposed and unexposed regions. Diffusion spreads the photoacid near the interface resulting in smoother features, but excessive chain length leads to line-edge-roughness (LER). LER can be improved by introducing a base to the system which neutralizes the excess acid near interface, which in turn reduces the sensitivity. A system with the optimal line-edge roughness, resolution and sensitivity is required [2, 4].

As the technology gears towards shorter exposure wavelengths, the transparency requirement led the resist film thicknesses to be in sub-100 nm range, a regime where interfacial phenomena plays a prominent role. Dynamic properties of ultra thin polymer films are influenced by the length scale, free surface and substrate interactions [5].



Figure 1.2: Image formation in positive CA resist systems: Irradiation converts the PAG into a strong acid, which diffuses through the resin matrix and reacts with the protective pendant group resulting in polarity switch.

### 1.2 The Bottom-up Process

Directed assembly of thin films of block copolymers on chemical patterns offers the possibility of improving the capabilities of lithographic processes due to its ability to transfer the pattern period, feature shape and registration from the lithographic pattern at the same time enhances the critical dimension control, LER and resolution. Self-assembly relies on thermodynamics to generate the image, rather than the complex reaction-diffusion mechanism in chemical amplification.



Figure 1.3: Directed self-assembly of block copolymers on an epitaxial template.

Image formation in directed-self assembled block copolymers is controlled by the the orientation of the self-assembled pattern with respect to the substrate surface as illustrated in Figure 1.3. The pattern orientation is determined by the relative strength of the surface affinity of each block [6]. Therefore the formed images are determined by the size and the quality of the lithographically defined surface pattern [7].

#### 1.3 Motivation

The focus of this work is to develop x-ray diffraction (XRD) techniques to characterize the formed nanostructures in our top-down and bottom-up model systems. X-ray diffraction techniques are sensitive to spatial variations of electron density. Therefore this technique can be applied to periodic structures such as line gratings or dot arrays where there is an electron density change.



Figure 1.4: Our goal is to measure the depth dependant image resolution in thin polymeric films with small angle x-ray scattering. Depth sensitivity is attained by varying the  $\phi$  angle.

At present, the CA resist process design relies heavily on simulating the exposure, image formation and development processes. There are no metrologies that provide direct feedback for the image formation mechanism, so process optimization requires predictive and quantitative models for CA resist chemistry that consider complex physical and chemical parameters such as acid diffusion, LER, surface/interface interactions, and polymer size effects. By modeling the diffraction data, the image resolution, shape and the structure of the deprotection interface can be calculated with nanometer accuracy. There are currently no experimental methods available to directly measure the latent image of these nanostructures, therefore the information obtained can be used to identify the fundamental limitations of chemical amplification for the next generation lithography.

The current research on directed assembly primarily analyzed the patterns formed on the free surface of the film using top down and cross sectional two dimensional microscopic images. Even though microscopic imaging provides useful information on the assembled domain shapes, small imaging area, complex sample preparation makes the imaging process tedious. XRD techniques provide the advantage of large area measurements and a simple sample preparation process.

#### 1.4 Overview

This dissertation discusses our approach to measure the depth dependent resolution of nanostructures in polymeric thin films. We introduce our model chemically amplified resist system in Chapters 2 to 10, followed by the directed self-assembly in Chapter 11.

Chapter 2 provides an introduction to our model chemically amplified resist system. The resist chemistry is detailed. The underlying exposure chemistry in nearultraviolet wavelengths and extreme-ultraviolet wavelengths is explained. Chapter 3 discusses the physics of image formation in thin CA resist films. The factors that contribute toward the free volume distribution is detailed. Finally, some of the common challenges in CA resist systems such as segregation of the photoacid generator and environmental contamination is discussed.

Chapter 4 explains the thermal characteristics of the copolymer system. This chapter explains the principles of spectroscopic ellipsometry and infrared spectroscopy, and the application of the above techniques to measure the thermally induced deprotection and the glass transition temperature of thin films of our copolymer system.

Chapter 5 discusses the approach we employed to determine the "bulk" kinetic and the transport parameters of our model resist system. Characterization of the level of deprotection with infrared spectroscopy is presented. The appropriateness of anomalous diffusion with subdiffusive transport is discussed.

Chapter 6 explains the sample preparation process for small angle x-ray scattering measurements. This chapter includes the details on substrate preparation, nanopatterning and post exposure processing, followed by a discussion on the optimization of process variables.

Chapter 7 gives an overview of the lithography process. Electron beam lithography, which we used to generate our nanopatterns is detailed. The factors that affect the pattern resolution is detailed. Finally, optimum patterning conditions for our samples is discussed.

Chapter 8 and Chapter 9 detail the theory of x-ray diffraction techniques that are applicable for our measurements. The concept of x-ray reflectivity is presented in Chapter 8, followed by the experimental protocols and the measured scattering length densities for our post exposure bake conditions. Chapter 9 details small angle x-ray scattering principles, introduces the reciprocal space, details the calculations of the line shape function and the interface function and discusses the two data modeling approaches we employed.

Chapter 10 presents our key results for the chemically amplified resist system. We detail the scattering data analysis procedure and present our results in this chapter.

Chapter 11 discusses the measurement of the 3-dimensional structure of the direct self-assembled block copolymer domains. This chapter explains our scattering based analysis, presents the calculated domain shapes and our mean field theory simulation based approach to interpret the experimental results.

Chapter 12 addresses the conclusion and outlook. This chapter highlights our key results and the applications of our novel approach in characterizing image formation in polymeric thin films.

Chapter 13 titled "Spatial Coherence in Electron-Beam Patterning," explains an x-ray diffraction based methodology we employed to extract the external "noise" amplitudes and frequencies in electron beam patterning. This is a simple technique which does not require complex data modeling.

#### Chapter 2 Introduction to Chemically Amplified Resists

This chapter introduces our model chemically amplified resist system and illustrates the underlying chemistry of exposure. Our model system is a positive CA resist system which consists of a polymer with an acid labile pendant group, photoacid generator and an optional base additive. Exposure to radiation, generates the photoacid. When heated at moderate temperature, the photogenerated acid diffuses and cleaves the pendant group (or deprotects) to a carboxylic acid, which then can be washed away using a polar solvent [1].

#### 2.1 Chemistry

#### 2.1.1 Resin Matrix

The random copolymer resin was poly(4-hydroxystyrene-*co-tert* butylacrylate), 40% poly(*tert*)butylacrylate by volume, supplied by DuPont Electronic Materials, with a molecular weight  $M_n = 10.4$  kg/mol and a polydispersity index of 1.8 (Figure 2.1). The "bulk" glass transition temperature of this polymer is reported as 140°C [1]. The polymer can undergo two competing deprotection reactions: thermal deprotection and acid-catalyzed deprotection.



Figure 2.1: Deprotection reaction of the copolymer resin.

#### 2.1.2 Photoacid Generator (PAG)

The photoacid generator (PAG) being used is triphenylsulfonium perfluoro-1butanosulfonate (Sigma Aldrich) with a molecular weight of 562.46 g/mol<sup>-1</sup> is illustrated in Figure 2.2. Exposure to radiation (ultraviolet, electron beam or x-ray) generates a strong Brönstead acid,  $H^+[CF_3(CF_2)_3SO_3]^-$ . This acid's film quantum yield at 13.5nm wavelength is 2.08, while at 248nm it is 0.33 [8].



Figure 2.2: Brönstead acid generation reaction of the photoacid generator Triphenylsulfonium perfluoro-1-butanosulfonate.

#### 2.1.3 Base Quencher

Diphenylamine with a molecular weight of  $169.22 \text{ gmol}^{-1}$  with a boiling point of  $302^{\circ}$ C and a very low vapor pressure (1 mm Hg at 108 °C) is used as a base additive (Figure 2.3(a)). A low vapor pressure base additive is needed to ensure that it doesn't evaporate during the reaction.



Figure 2.3: (a) Base quencher - Diphenylamine and (b) Solvent - PG-MEA.
#### 2.1.4 Solvent

The above three components in the system are soluble in propylene glycol methyl ether acetate (PGMEA), which is used as a solvent (Figure 2.3(b)). PGMEA has a density of 0.97 g/ml and a boiling point of  $145^{\circ}$ C. The vapor pressure of PGMEA is 3.7 mmHg at room temperature.

# 2.2 Deprotection Reaction

The copolymer can be deprotected by two competing pathways: at elevated temperatures the polymer undergoes thermal decomposition, and also the decomposition reaction can be activated and propagated by catalysis. At high enough temperatures both pathways can compete with each other, however thermally induced deprotection is much slower than the acid catalyzed deprotection rate.

#### 2.2.1 Thermal Deprotection

Thermal deprotection of the polymer can be described by the process below [9]:

$$tBA \xrightarrow{\kappa_1} AA + products,$$
 (2.1)

$$tBA + nAA \xrightarrow{\kappa_2} (n+1)AA + products.$$
 (2.2)

This is an autocatalytic reaction in which the reaction products act to increase the overall rate of reaction. The small organic molecules produced by the deprotection reaction are volatile and thus diffuse toward the top of the film surface. The diffusion of these can be explained in a similar mechanism as the photoacid and base diffusion. Therefore, the rate of reaction can be written as,

$$\frac{-dA}{dt} = k_1[A] + k_2[A][B]^n.$$
(2.3)

#### 2.2.2 Acid-catalyzed Deprotection

At near and mid ultraviolet lithography, photons are directly and selectively absorbed by the photoacid generator. With the reduction in UV wavelength towards extreme ultraviolet (EUV), x-ray and electron beam wavelengths the absorption of radiation by the polymer matrix becomes the dominant mechanism.

Imaging chemistry of the model system in near - mid ultraviolet wavelengths: irradiation results in a proton which binds to the ester group which causes the ester to be replaced with a carboxylic acid. The unstable by-product, the carbocation, releases a proton which then protonates another ester group acting as a catalyst (Figure 2.4) [2].



Figure 2.4: Imaging chemistry of near and mid-UV wavelengths: Irradiation of PAG generates an acidic product. The so formed proton binds to the protective pendant group which induces fragmentation to generate the carboxylic acid, which is the deprotected product and the proton is regenerated.

Imaging chemistry in extreme ultraviolet, x-ray and electron beam wavelengths was proposed by Kozawa [10]: The radical cations and electrons are generated by the ionization (as a result of absorption of radiation) of the phenolic component of the matrix,

$$MOH \to MOH^{+} + e^{-}.$$
 (2.4)

Ion molecular reactions generate photon adducts of the phenolic resin,

$$MOH^{+} + MOH \rightarrow MOH_2^+ + MO^{-}.$$
 (2.5)

Photoacid generator scavenge the above generated electrons,

$$e^- + RX \to X^- + products.$$
 (2.6)

Due to the slow mobility of the dissociated anions, they recombine with the proton adducts of the resin to form Brönsted acids, but at a much slower rate,

$$X^{-} + MOH_{2}^{+} \rightarrow HX + MOH.$$
(2.7)

Due to the presence of several kinds of proton donors, the reaction mechanisms become very complicated. But three dominant reactions at the post exposure bake can be highlighted:

(a) Protonation occurs directly from Brönsted acids,

$$HX + MOH \to MOH_2^+ + X^-, \qquad (2.8)$$

$$\mathrm{HX} + \mathrm{A} \to \mathrm{AH}^{+} + \mathrm{X}^{-}, \qquad (2.9)$$

where A is the pendant group.

(b) Protonated adducts are formed by the attachment of the protons formed by HX dissociation:

$$\mathrm{HX} \rightleftharpoons \mathrm{H}^+ + \mathrm{X}^-, \tag{2.10}$$

$$\mathrm{H}^{+} + \mathrm{MOH} \to \mathrm{MOH}_{2}^{+}, \qquad (2.11)$$

$$\mathrm{H}^{+} + \mathrm{A} \to \mathrm{A}\mathrm{H}^{+}.\tag{2.12}$$

(c) Proton adducts of the base polymer protonates the protective pendant group,

$$MOH_2^+ + A \to AH^+ + MOH. \tag{2.13}$$

The so formed protonated cleavage group decomposes as the reaction proceeds releasing the proton [10].

# 2.3 Summary

For better understanding of our model system, we performed experiments to measure the extent of thermal and acid catalyzed deprotection using spectroscopy techniques. Chapter 4 discusses the contribution of thermal deprotection at lower annealing temperatures which is of importance in molecular level simulations. Determining kinetic and transport parameters of the acid catalyzed reaction requires better knowledge of the deprotection mechanisms.

# Chapter 3 Image Formation in Chemically-Amplified Resist Thin Films

To ensure the UV transparency, the thickness of the photoactive layer should be at the sub 100nm range. The behavior of these thin films can differ from the "bulk" or thick film behavior due to several factors, such as interfacial interactions and thin film confinement. Since the discovery of the thickness dependence of the glass transition temperature, there has been a wide interest in understanding the above phenomena in this confined films. The importance of the above to the lithography community lies mainly in the post apply bake (PAB) and post exposure bake (PEB) processes. In thin films typical PAB and PEB temperatures are about  $40 - 50^{\circ}$ C below the bulk  $T_{\rm g}$  of the polymer.  $T_{\rm g}$  depression can lead to acid diffusion between exposed and unexposed regions resulting in image blur [11]. Many factors contribute to the size, shape and the roughness of the latent image including the segregation of photoacid generator molecules and other additives, diffusion of the photoacid at the interface, outgassing during deprotection reaction, thickness effects, the extent of deprotection at the interface etc. With the shrinking size of the patterns, lithography will become increasingly affected by the surface phenomena, substrate interactions and confinement issues which can affect the formed latent image. This chapter discusses the factors that influence the image formation process in polymer thin films.

# 3.1 Diffusion in Polymer Thin Films

Diffusion is a sequence of random movements of the diffusant relative to its environment. When the diffusant is spatially segregated resulting in a concentration gradient within the polymer matrix inducing the diffusant to spread from higher concentration to the lower, spreading over the accessible volume until it is homogeneously distributed. Thus the rate of diffusion is strongly influenced but not limited by the degree of spatial segregation and the availability of free volume [12, 13]. The acid catalyst (PAG) in the resist film has a spatially nonuniform distribution, which results in initial gradients in the local concentrations of the photoacid at irradiation. As the post exposure bake (PEB) step proceeds, the polymer matrix become mobile generating the free volume, where the spatial distributions of the photoacid, reactions and the deprotection products evolve transforming the initial image [2].

An atom or molecule must have a vacant volume available in order to move from one location to another. Such voids are created transiently in a polymer through fluctuations in the chains. Therefore, the magnitude of the diffusion coefficient depends of the size of the diffusant and on the range of motion in the polymer. When the polymer is undergoing decomposition, large density changes which are not instantaneous exist, which affects the available free volume within the matrix, resulting in a diffusion coefficient that varies with conversion [12–15].

Two factors that play an important role in diffusivity in the sub-100 nm film thicknesses are the surface and substrate interactions and polymer confinement. As the length scales approach to the unperturbed dimensions of the polymer molecule, the confinement induced deviations in the physical properties such as glass transition temperature ( $T_g$ ) and spinodal dewetting play a significant role. The influence of a substrate on polymer dynamics vary with the nature of the polymer-substrate interactions [16,17]. Favorable interactions result in the polymer segments being immobile at the substrate increasing  $T_g$  (Figure 3.1). The dynamics at interfaces can impact the  $T_g$  tens of nanometers into the film, leading to a distribution of free volume that strongly depends on thickness [18]. The average diffusivities in thin films typically decrease by an order of magnitude due to the influence of an attractive substrate [19].



Figure 3.1: Hydrogen bonding between hydroxystyrene and a silicon substrate (Tate et.al,2001).



Figure 3.2: Diffusivity of PFOS into PBOCST increases with film thickness (Goldfarb et.al,2001).

Soles et al. reported that the interactions between polyhydroxystyrene and the substrate are greater for the silicon nitride surface than silicon dioxide surface based on the magnitude of the thermal expansion coefficients [11]. A reduced thermal expansion coefficient corresponds to reduced molecular mobility, which impacts photoacid diffusion, dissolution as well as reactive-ion etching. It has been observed that the photoacid diffusivity is increased with film thickness [20]. Figure 3.2 illustrates the change in Di(t-butylphenyl) iodonium perfluorooctanesulfonate (PFOS) photoacid diffusivity into p-tert-butoxycarboxystyrene (PBOCST) films as a function of film thickness which is illustrated in Figure 3.2. The catalyst is a proton which does not exist in isolation. The transport of the catalyst involves a series of transfer from one void to another. The accessibility of each proton transfer path, whether a direct transfer between two close pendant groups or from a pendant group to a small molecule and back to a pendant group is determined by the proton affinity of each of the above paths. However, in order to maintain the electrical neutrality within the system, the proton cannot move much further from its counterion, which had the same spatial distribution as the proton at irradiation [2]. Therefore, it has been reported that by varying the size of the counterion of the PAG system, the level of deprotection as well as the line-edge roughness can be controlled [15]. A larger counterion can reduce the catalyst chain length, slow down the rate of deprotection and reduce LER.

# **3.2** Other Factors

#### 3.2.1 PAG Segregation

Most of the PAGs that are being used in the industry are fluorinated. These fluorinated molecules have lower surface energy than the polymer, so they tend to segregate towards the free surface of the film. NEXAFS studies by Lenhart et al, observed bis(p-tert-butylphenyl) iodonium perfluoro octanesulfonate photoacid generator (PFOS) segregation at the resist-air interface of the poly(tert-butyloxycarbonyloxy-styrene) polymer (PBOCSt) resin (Figure 3.3) [21]. The surface segregation leads to a higher acid content, therefore faster deprotection reaction at the air-polymer interface with respect to the bulk of the film.

#### 3.2.2 Acid-base Interactions

It is being reported that an added base into the system serves multiple purposes in image formation [2]. A very important factor is that the base neutralizes the



Figure 3.3: Surface NEXAFS spectra from PBOCSt/PFOS film. The fluorine peaks are strongly observed in the NEXAFS spectrum which are not present in the fluorescence yield spectrum of the bulk sample at the inset (Lenhart et.al,2005).

"background" acid generated as a result of the diffraction of light, which otherwise could deprotect the unexposed areas resulting in image blur. Any base remaining in the unexposed regions act as traps for acid diffusion generating a barrier that inhibits image blur and reduces line edge roughness.

The overall rate of neutralization in each area of the film can be described as,

$$\mathbf{R}_{\mathbf{n}} = \mathbf{k}_{\mathbf{n}} \ [\mathbf{A}] \ [\mathbf{B}], \tag{3.1}$$

where  $k_n$  being the neutralization rate constant at a given temperature, and [A] and [B] are the instantaneous local concentrations of the acid and the base respectively. However, the role of the added base is very much dependent on the specific base quencher [19].



Figure 3.4: (a) T-topping due to contamination by airborne base quenchers. (b) AFM micrograph of a contaminated sample.

Another advantage is that an added base in sufficient quantities could reduce the levels of airborne contamination by neutralizing the excess surface acid levels resulting from photoacid segregation. Airborne quenchers can neutralize the acid at the top of the film resulting in t-topping, where the level of deprotection at the air interface is much lesser than at the bulk of the film as shown in Figure 3.4.

# Chapter 4 Thermal Characteristics

In order to better understand the mechanistic details of the post exposure bake step, we performed a series of experiments to characterize the thermal properties of our model copolymer. Our key emphasis was to determine the glass transition temperature of copolymer thin films and to understand the significance of the thermally induced deprotection as a function of temperature. We employed spectroscopic ellipsometry to evaluate the glass transition temperature, while a combination of infrared spectroscopy and ellipsometry was used to estimate the thermal deprotection.

## 4.1 Spectroscopic Techniques

Spectroscopy is a non-destructive technique used for both qualitative and quantitative evaluation of materials. The concept comprises of any interaction with radiative energy as a function of wavelength.

#### 4.1.1 Spectroscopic Ellipsometry

Spectroscopic ellipsometry is an optical technique used for analysis and metrology. It measures the change in polarization as light reflects or transmitts from a material structure. The change in polarization is expressed by the amplitude ratio  $\Psi$  and the phase difference  $\Delta$ . The output depends on the optical properties of the material as well as the thickness.

Optical properties of a material are expressed by its complex refractive index  $\tilde{n}$ ,

$$\tilde{\mathbf{n}} = \mathbf{n} + \mathbf{i}\mathbf{k},\tag{4.1}$$

where n is the index and k is the extinction coefficient.

The index describes the phase velocity  $\nu$  of light as it travels in the material with respect to the speed of light in vacuum (c), whereas the extinction coefficient describes the loss of wave energy (absorption coefficient,  $\alpha$ ) to the material as:

$$\nu = \frac{c}{n}, \tag{4.2}$$

$$\alpha = \frac{4\pi k}{\lambda}.$$
 (4.3)

In ellipsometry a known polarization is incident on the sample and the output polarization is measured. The light source produces unpolarized light which is then sent through a polarizer. The polarizer axis is oriented between the p- and the splanes such that both p-polarized and s-polarized light arrive at the sample surface. The polarized light that reflects from the sample surface is elliptically polarized which then travel through a continuously rotating polarizer (which is the analyzer), which converts the light to an electronic signal to determine the reflected polarization. Comparing the above with the incident polarization results in the change that result due to the reflection by the sample.

The change in polarization can be expressed by,

$$\rho = \tan(\Psi) e^{i\Delta}. \tag{4.4}$$

A model is used to calculate the predicted response from Fresnel's equations which describes the optical constants and the thickness of the material. Since the resist material being used is transparent Cauchy's equation and Sellmeier's equation were used to determine the thickness of the films,

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}.$$
(4.5)

Cauchy's equation is described in Equation 4.5 where  $n(\lambda)$  is the refractive index A, B, C are material specific coefficients and  $\lambda$  is the wavelength.

Sellmeier equation handles anomalously dispersive regions, therefore more accurately describes the materials refractive index over visible and infrared regions. For glass like materials,

$$n^{2}(\lambda) = 1 + \frac{B_{1}\lambda^{2}}{\lambda^{2} - C_{1}} + \frac{B_{2}\lambda^{2}}{\lambda^{2} - C_{2}} + \frac{B_{3}\lambda^{2}}{\lambda^{2} - C_{3}}.$$
(4.6)

Finding the best fit between the model and the experiment is done by the use of regression, and the mean square error (MSE) is used to quantify the deviation. Ellipsometry is capable of measuring film thicknesses from sub-nanometer range to a few microns. As films become thicker than several tens of microns, interference oscillations become very difficult to resolve. In addition, thickness measurements require a portion of light to trave through the entire film and return to the surface, therefore, if the material absorbs light, thickness measurement will be limited to thin semi-opaque layers. Typically the absorbing materials have a transparent wavelength region that can be modeled using Cauchy or Sellemeier models.

Ellipsometry was primarily used to measure the film thickness of the samples and to estimate the thermal deprotection reaction in the resist system. All experiments were carried out in the absence of the ultraviolet region of light.

#### 4.1.2 Infrared Spectroscopy

Infrared (IR) spectroscopy measures the vibrational energy levels of molecules. Absorption of IR energy results in stretching, contracting and bending of chemical bonds. Vibrational levels are distinctive for each molecule due to structural differences, therefore an IR spectrum describes the characteristics of a molecule. Interaction of the electric vector of an electromagnetic wave with matter produce infrared absorbance. When the alternating polarity electric vector reaches a dipole moment, depending on the polarity of the electric vector at the vicinity of the respective molecule the bond length of a dipole moment increase or decrease alternatively. During this precess the molecule vibrates at the same frequency as the electric vector, and the IR energy is transferred to the molecule.

One necessary condition for a molecule to absorb IR radiation is that it should vibrate during which the change in dipole moment with respect to distance is nonzero. That is  $\partial u/\partial x \neq 0$  needs to be satisfied, where  $\partial u$  and  $\partial x$  are the change in dipole moment and change in bond distance respectively. Vibrations that satisfy this equation are "infrared active" and results in absorption bands in an infrared spectrum. Inversely, molecules can possess vibrations for which the change in dipole moment with respect to the bond distance is zero, which are "infrared inactive". For example in CO<sub>2</sub> molecule, if the oxygen atoms are pulled away from the carbon atom symmetrically, the oxygen atoms are always at the same distance from the carbon canceling the net vibration. Therefore the symmetric stretch of CO<sub>2</sub> does not result in a infrared band, and so does the homonuclear diatomic molecules. In addition, the intensity of the IR band is proportional to  $(\partial u/\partial x)^2$ 

The second necessary condition is that based on quantum mechanics the energy of the light impinging on a molecule must equal a vibrational energy level difference within the molecule. i.e.,  $\Delta E_{vib} = hcW$ , where  $\Delta E_{vib}$  is the vibrational energy level difference in a molecule, h is Planck's constant, c is the speed of light and W is the wavenumber in cm<sup>-1</sup>. If the photon energy which is equal to hcW satisfies the equation above, it will be absorbed by the molecule while the opposite being transmitted.



Figure 4.1: A hypothetical plot of potential energy of a molecule vs. bond distance for a given X-Y bond.

Figure 4.1 illustrates a plot of potential energy with bond distance. At room temperature, most molecules are in the ground vibrational state (v=0). If the absorption of infrared radiation results in the excitation to the first vibrational energy level (v=1), it is said to have undergone a fundamental transition. Most of the molecules have vibrations for which the v=1 level is 4000 - 400 cm<sup>-1</sup> in energy greater than the v=0 energy level. Therefore these give rise to bands in the infrared region 4000 - 400 cm<sup>-1</sup> in which range most of the mid infrared instrument operates. Fundamental transitions are the strongest bands in an IR spectra.

#### IR Peak Positions, Intensities and Widths

**Peak Position** The frequency of vibration (peak position) is only affected by the chemical bond's force constant and the reduced mass, which determines the wavenumber at which a molecule will absorb IR radiation. Therefore the IR spectrum of each substance is unique. There are external factors that affect the force constant of the molecule and influence the peak position such as temperature, pressure, physical state and chemical interactions.

**Peak Intensity** A factor that determines the peak intensities is the concentration of molecules in the sample. According to Beer Lambert's law with an absorbance A, absorptivity  $\varepsilon$ , path length l and concentration c,

$$\mathbf{A} = \varepsilon \mathbf{lc.} \tag{4.7}$$

The optical path length is the sum of the product (Nt) with N being the refractive index of the part and t being the length of the portion, therefore dependant on film thickness.

**Peak Width** The chemical environment of the molecule (intermolecular interactions) play a major role in determining the peak width. Broad IR bands are observed for samples with more chemical environments. In a sample with hydrogen bonding, the number and strength of intermolecular interactions vary greatly within the sample resulting in much broader bands. Typically solids and liquids display broader peaks of about 8 - 10 cm of Gaussian or Lorentzian shapes, whereas gas phase spectrums exhibit much sharper peaks (< 1 cm).

#### **Brewster's Angle**

When a light beam is incident at a plane parallel surfaces of a transparent sample, the constructive and destructive interference from the partial reflection gives rise to interference fringes. The factors that influence this phenomena are the incident wavelength, incident angle and the thickness of the transparent film. Interference fringes are very useful in the measurement of film thickness and refractive index, construction of interference filters, cold mirrors and modulation of light [22]. In optical spectroscopy, these fringes obscure weak absorption bands making the analysis difficult. However it is possible to obtain a fringe free transmission spectra as described below:



Figure 4.2: Schematic illustrating the requirements for fringe free spectra.

When an electromagnetic wave encounters a dielectric material, at a particular angle the polarization effect of the interaction becomes maximum, which is the Brewster's angle. The interaction can be polarization and reflection of unpolarized energy or the cancelation of energy through absorption.

Brewster's angle is consistent for incident light and the dielectric materials with similar characteristics. However it varies with the wavelength of radiation and the refractive index of the dielectric material. **Brewster's Law** According to Snell's law, the refracted portion of the transmitted light is described as  $n_1 \sin \theta = n_2 \sin \alpha$  and for the reflected beam, the angle of reflection is equal to the angle of incidence (Figure 4.3).



Figure 4.3: Refraction and transmission of a light beam at a media.

Fresnel's equations describe the reflected amplitudes for perpendicular and parallel polarization where the electric field vector vibrates in the plane perpendicular and parallel [22],

$$\mathbf{r}_{\perp} = -\frac{\sin(\alpha - \theta)}{\sin(\alpha + \theta)},$$
(4.8)

$$\mathbf{r}_{\parallel} = \frac{\tan(\alpha - \theta)}{\tan(\alpha + \theta)}.$$
 (4.9)

For parallel polarization, the reflectivity  $R_{\parallel}(r_{\parallel}^2)$  decreases at first with the increasing angle of incidence and becomes zero at Brewster's angle,  $\theta_B = \tan^{-1}n_{12}$ . Since  $\tan(\theta_B + \alpha_B) = \tan 90^\circ$  at this angle,  $R_{\parallel}$  becomes zero [23].

# 4.2 Measurements of Thermal Deprotection

#### 4.2.1 Experimental

Ellipsometry Experiments This experiment was carried out in J.A.Woolam spectroscopic ellipsometer. 4 wt% copolymer solution in PGMEA was spun on piranha cleaned single side polished p-type(100) silicon substrates, the obtained film thickness was  $\sim$ 100nm. The film was then baked in a shielded hot plate at 130°C for 2 min for solvent evaporation. Using the ellipsometer heat stage, in-situ film thickness vs. time measurements were taken at each of the four temperatures, 170°, 175°, 178° and 180 °C.

For in-situ measurements, a heat stage in an inert Ar environment was used. The sample was quickly ramped to the given temperature with a ramping time of < 1 min, and let it remain for a given time.

**IR Spectroscopy Experiments** The substrates were piranha cleaned double side polished p-type(100) silicon wafers. IR spectra was obtained from poly(4-hydroxystyrene) and poly(tert-butylacrylate) homopolymers and the PHOST-PtBA copolymer for reference. The samples were prepared by spin casting the polymer solution and post apply baking 2 mins at 130°C. The samples were annealed overnight at 180°C in a vacuum oven so that the copolymer and the tert-butylacrylate polymers were thermally deprotected. Poly(4-hydroxystyrene) homopolymer was annealed at the same conditions to verify its thermal stability. IR spectra were taken from all samples before and after annealing for comparison. To examine the level of thermal decomposition at low annealing temperatures a 10 wt% copolymer solution in PGMEA was spun on clean substrates, post apply baked, and annealed at 70°, 80° and 90° for 20 hrs, 6 hrs and 4 hrs respectively. IR measurements were taken before and after annealing.

IR absorbance was measured with a Nicolet NEXUS 670 FTIR spectrometer equipped with a Brewster angle sample stage. Samples were measured in transmission mode with an incident angle of 16°, which is near the Brewster angle of the silicon substrate. IR absorbance was recorded with OMNIC data acquisition software at a resolution of 8 cm<sup>-1</sup> with an average of 128 scans, for a better signal-to-noise ratio.

#### 4.2.2 Results

It can be noted that the *tert*-butylacrylate bulk ester group gets converted to acrylic acid, and the volatile organic compounds escape from the film resulting in volume loss in the film as the reaction proceeds. The volume loss fraction due to deprotection can be calculated as,

$$V_{fl} = \frac{V_{ini} - V}{V_{ini}}.$$
 (4.10)

It can be observed from Figure 4.4 that the  $V_{fl}$  increases with increasing temperature but eventually reaches a constant plateau.

As the annealing temperature is reduced the rate of change of  $V_{fl}$  slows down, indicating a slower rate of reaction (Figure 4.4). Therefore, the film thickness loss measured by ellipsometry at a given temperature can be related to the level of deprotection. Thermal decomposition plays an important role at higher temperatures, however IR spectroscopy results presented below indicate that at much lower temperatures (30 - 40°C below  $T_g$ ) there is no detectable thermal decomposition.



Figure 4.4: The calculated volume loss fraction eventually reaches a plateau. (a) For a 100 nm film at different temperatures. (b) The rate of change in volume loss fraction as a function of film thickness at  $175^{\circ}$ C.

The reference IR spectra in Figure 4.5(b) and Figure 4.6 displays the spectra of the protected and the deprotected polymers. It is apparent that the peaks at 1149 cm<sup>-1</sup>, 1369 and 1390 cm<sup>-1</sup> and 2977 cm<sup>-1</sup> in tert-butylacrylate and the copolymer disappear at 100% deprotection level. No apparent change was observed in the poly(hydroxystyrene) after thermal annealing. It could also be seen that the peak positions near 1200 - 1270 cm<sup>-1</sup> were shifting due to Hydrogen bonding.



Figure 4.5: IR spectra of (a) poly(hydroxystyrene) and (b) poly(tertbutylacrylate) homopolymers before and after bake at  $180^{\circ}$ C in a vacuum oven for 15 hrs.

Figure 4.7 presents the IR spectra of the copolymer were annealed on a shielded hotplate at 70°, 80° and 90°C for longer times. The spectra before and after indicate that there is no thermal deprotection at low anneal temperatures.



Figure 4.6: IR spectra of the copolymer poly(hydroxystyrene-co-tertbutylacrylate) before and after thermal deprotection at  $180^{\circ}$ C in a vacuum oven.



Figure 4.7: Reference IR spectra for the copolymer annealed at (a)  $70^{\circ}$ C for 20 hrs (b)  $80^{\circ}$ C for 6 hrs (c)  $90^{\circ}$ C for 4 hrs.

# 4.3 Glass Transition Temperature $(T_q)$

Measurement of  $T_g$  of the copolymer was challenging due to its thermal instability at higher temperatures. Copolymer films of 100 nm and 32 nm were spun casted and post apply baked before ellipsometry measurements. The bulk  $T_g$  for this system is reported to be 140°C [1]. Considering the rate of thermal deprotection calculated from the results above a temperature range of 90° - 150°C was adopted for the experiment.



Figure 4.8: Ellipsometry film thickness measurement vs. temperature.

Figure 4.8 illustrates the measured film thickness as a function of heating / cooling temperature for a 100 nm copolymer film. The reduction in thickness at each cycle indicates the thermal instability of the copolymer. Glass transition temperature at each heating and cooling cycle was calculated by determining the intersection between two asymptotes drawn at the glassy and the melt regions (Figure 4.9(a)). The calculated  $T_g$  values for each temperature cycle for two films of 100 nm and 32 nm thickness are presented in Figures 4.9(b) and (c) respectively. It can be observed that the  $T_g$  values are higher in the 32 nm film, indicating the presence of polymer-substrate interactions. For both film thicknesses the  $T_g$  range from 137°C - 140°C.



Figure 4.9: a) Example of  $T_g$  measurement for a 100 nm thick PHOST-PTBA film. The calculated  $T_g$  (b) for a 100 nm film and (c) 32 nm film increases with the number of heating/cooling cycles due to the slow, thermally-activated deprotection of tBA.

# Chapter 5 Reaction kinetics in acid-catalyzed deprotection of polymer films

A quantitative description of kinetics in acid-catalyzed polymer deprotection reactions requires proper identification of the controlling mechanisms. We examined the acid-catalyzed deprotection of a glassy poly(4-hydroxystyrene-co-tertbutyl acrylate) resin using infrared absorbance spectroscopy and stochastic simulations. We interpret experimental data with a model that explicitly accounts for acid transport, while heterogeneities at local length scales are introduced through a non-exponential distribution of waiting times between successive hopping events. A subdiffusive behavior with long-tail kinetics predicts key attributes of the observed deprotection rates, such as a fast initial deprotection, slow conversion at long times, and a nonlinear dependence on acid loading. Most importantly, only two parameters are introduced to offer a near-quantitative description of deprotection levels at low acid loadings and short times. The model is extended to high acid loadings and long times by incorporating a simple acid depletion model based on mutual encounters. Our study suggests that macroscopic deprotection rates are controlled by acid transport in the glassy deprotected polymer, which presents with a strongly non-Fickian behavior.

# 5.1 Introduction

The most sophisticated integrated circuits, such as microprocessors and memory chips, are patterned with projection lithography. The efficiency of semiconductor devices is controlled by lithographic resolution (minimum feature size  $R_{min}$ ). To keep pace with historic growth rates (Moore's Law), future lithographic processes must resolve features at the scale of 10 nm [24]. Imaging materials for next-generation lithography must satisfy a number of demanding requirements, such as nanoscale resolution, near-perfect pattern uniformity, and high sensitivity to radiation [25]. The most sensitive resists are based on a process called chemical amplification [26–28]. Chemically-amplified (CA) resists have two principal components: (i) A lipophilic polymer with acid-labile protecting groups; and (ii) a low concentration of photoacid generator (PAG). Exposing the resist to radiation generates a strong acid catalyst, and heating at moderate temperature promotes the acid-catalyzed decomposition of protecting groups along the polymer backbone. This deprotection reaction changes the polymer polarity for development in an aqueous base. CA systems are highly efficient because each photon absorbed by the resist generates ca. 0.3-3 acids [29,30], and each acid cleaves hundreds of bonds [26], so a low radiation dose is "amplified" through chemistry. However, the excellent sensitivity of CA resists comes at a price, because catalytic efficiency and/or acid diffusion will limit the pattern resolution and uniformity [2,24,25,31,32].

There is a clear need to develop quantitative models of chemical amplification that can predict the spatial extent-of-deprotection with nanoscale resolution. It is well-established that deprotection kinetics are controlled by acid catalyst diffusion [2,31], but the mechanism cannot be described by simple Fickian transport models [33–35]. Macroscopic models have been proposed that include thermodynamic equilibria, free volume generation, acid trapping reactions, or concentrationdependent diffusion coefficients [36–40]. These studies aim to capture certain aspects of the deprotection reaction kinetics, such as the fast initial conversion or slow conversion at long times. For example, introducing concepts from polymer physics, Croffie et al. described an initially fast deprotection rate that is concurrent with the creation of free volume from escaping volatile by-products [37]. The additional free volume subsequently relaxes, leading to a dense polymer resin that arrests the acid mobility. A different route describes the overall deprotection rate as series of thermodynamic equilibria between the acid catalyst and protected or deprotected polymer [31]. Finally, many studies employ a phenomenological concentration-dependent acid diffusivity that increases with extent-of-deprotection [39, 41, 42]. In any case, it is unclear whether such descriptions can be extended to model material behavior at the nanoscale, where molecular parameters such as the distances between the reacting centers and acid-anion pair play a significant role [43]. To increase the challenge in capturing macroscopic behavior with a mesoscopic model, we note that local fluctuations in composition and density are anticipated [44], and it is not certain that mean values of parameters such as acid hopping times can adequately describe the transport mechanism in a reacting glassy polymer matrix.

Following a concerted modeling and experimental approach, we show that a surprisingly simple model of anomalous diffusive behavior can predict macroscopic deprotection rates. The model is based on an acid hopping process that presents a subdiffusive character, which generates extensive short-time reaction following by long-time limiting behavior. The model accurately predicts the higher-order dependence of deprotection rates on acid concentration.

Based on recent studies of anomalous diffusion in complex materials [45], we propose that deprotection rates are controlled by an underlying non-exponential distribution of acid hopping rates. We believe that our study provides a unique framework to examine the effects of polymer dynamics on reaction front propagation.

# 5.2 Experimental Procedures.

**Overview.** The aim of our experiments is to measure extent-of-reaction in a model chemically-amplified resist with infrared absorbance spectroscopy. The variables for

these experiments are catalyst loading, reaction temperature, and reaction time. Reaction temperature is always lower than the polymer's glass transition by at least 50 K. The following paragraphs describe four critical attributes of the experiments. First, we discuss the photoresist chemistry and deprotection mechanism. Second, we report the acid generation efficiency, which is an important parameter that determines the initial concentration of acid catalyst. Third, we describe the sample preparation for infrared absorbance spectroscopy. Finally, we provide protocols for analyzing spectroscopy data, where these data are used to quantify deprotection levels in the resist.

**Materials.** The materials used in this study are detailed in Section 2.2. All formulas were prepared by dissolving the polymer, PAG and/or base in propylene glycol monomethyl ether acetate. Substrates were double-side polished p-type (100) silicon wafers. Substrates were cleaned with Piranha solution (4 parts sulfuric acid, 1 part 30 wt% aqueous hydrogen perioxide), which destroys any organic contamination and makes the oxide surface extremely hydrophilic.

Acid Generation. The efficiency of acid generation was measured with the "standard addition" method, where known quantities of a base additive are added to the PAG/polymer blend, and the Dill C parameter is calculated from changes in critical dose due to base quenching [46–48]. Briefly, we prepared eight resist solutions of PHOST-PTBA, PAG, and base quencher. The polymer concentration in PGMEA was 10 wt% for all studies. The PAG loading was fixed at 4 wt% relative to PHOST-PTBA, but the molar ratio of base-to-PAG was varied from 0 to 0.69. Resist films were spun-cast on clean silicon wafers with a thickness of (280 ± 10) nm, and then baked at 130 °C for 2 min to remove residual solvent. Films were irradiated with 254 nm ultraviolet light (lamp power 1.74 mW/cm<sup>2</sup>) for different durations of time, where exposure time controls the dose delivered to the film (ca. 10–100 mJ/cm<sup>2</sup>). Films were baked at 90 °C for 30 sec to activate the acid–catalyzed deprotection reaction. Films were developed with an aqueous solution of 0.26N tetramethylammonium hydroxide (MF 319 by MicroChem) for 20 sec and rinsed with deionized water. The residual film thickness was measured as a function of exposure dose for each resist formula. Note that all resist thicknesses were measured with a JA Woollam M-2000 spectroscopic ellipsometer ( $\lambda = 190 - 1690$  nm). Ellipsometry data were modeled with the Cauchy dispersion relation  $n(\lambda) = A + B/\lambda^2$ , where A, B, and film thickness were adjustable parameters for regression analysis (all positive values). This model provides an excellent description of ellipsometry data in the range of 350–1690 nm. To fit the data in the deep ultraviolet range, we employed an Urbach tail that accounts for absorption.



Figure 5.1: Efficiency of acid generation (a) Contrast curve to find  $E_o$  (b) Calculating the Dill C parameter (mJ/cm<sup>2</sup>)

The first step of the "standard addition" technique is determining the critical exposure dose  $E_0$  for each resist formula, which is the radiation dose that makes the film soluble in the developer. The critical dose is readily identified from resist contrast curves, meaning plots of normalized residual thickness  $(h_f/h_0)$  as a function of dose E. These data are reported in Figure 5.1a. The second step is to plot the molar ratio of base-to-PAG ([B]/[PAG]) against critical dose  $E_0$ , and fit these data to a line. The slope of this line is the Dill C parameter without absorption corrections. Finally, the Dill C parameter including absorption corrections is

$$C = \text{slope} \cdot \frac{a}{1 - \exp(-a)},\tag{5.1}$$

where a is the film absorbance (base e). The absorption coefficient for the resist is  $\alpha = 4\pi k/\lambda$ , where k is the imaginary component of the refractive index and  $\lambda = 254$  nm is the wavelength of light. The total film absorbance is  $a = \alpha \ln(10)h_0$ . Figure 5.1b reports the outcomes of this experiment, where the key result in the value  $C = (0.043 \pm 0.001) \text{ cm}^2/\text{mJ}$ . The acid generation efficiency is calculated with the Dill equation,

$$[\mathrm{H}^+] = [\mathrm{PAG}]_0 \left(1 - \exp\{-CE\}\right).$$
(5.2)

Note that 99% of the PAG is activated when the radiation dose exceeds  $100 \text{ mJ/cm}^2$ .

**Deprotection Kinetics.** Resist formulas were prepared with PHOST-PTBA resin and PAG loadings of 1 wt%, 2 wt%, 4 wt% or 10 wt%. The polymer concentration in PGMEA was 10 wt% for all studies. Base quenchers were not included in these studies. Resist films were spun-cast onto clean silicon wafers with thicknesses of 250–300 nm, then baked for 2 minutes at 130 °C to remove residual solvent. Resist films were irradiated with 254 nm light at a dose of 150 mJ/cm<sup>2</sup>, which ensures that all PAG is decomposed into acid catalyst (efficiency > 99%). Each wafer was cut into smaller sections, so one piece was used to calibrate the initial concentration of protecting groups, while other pieces were annealed for different durations of time on a shielded hotplate at fixed temperature. The temperatures were 70 °C, 80 °C, or 90 °C, and the deprotection times were varied depending on acid loading and temperature. The temperatures were selected to achieve measurable deprotection levels within a reasonable time (less than 24 hours).

Fourier-Transform Infrared (IR) Spectroscopy. IR absorbance was measured with a Nicolet NEXUS 670 FTIR spectrometer equipped with a Brewster angle sample stage. Samples were measured in transmission mode with an incident angle of  $16^{\circ}$ , which is near the Brewster angle of the silicon substrate. IR absorbance was recorded with OMNIC data acquisition software at a resolution of 8  $\rm cm^{-1}$  with an average of 128 scans. The baseline was subtracted using a "point-and-click" procedure in Matlab, where the user identifies the minima in the spectra and the software fits a line to connect those points. The signal from a clean silicon wafer was subtracted from each PHOST-PTBA spectra. Table 5.1 reports the IR peak assignments for PHOST-PTBA [49, 50, 50]. The strongest signal associated with the protecting TBA groups is detected at 1149 cm<sup>-1</sup>. The absorbance is calculated by fitting the spectra in the range of 1134-1276 cm<sup>-1</sup> to a model based on four peaks. The peak centers were near 1151, 1172, 1240, and 1275  $\rm cm^{-1}$ , and peak line shapes were Gaussian, Lorentzian, Gaussian, and Gaussian, respectively. Each series of measurements includes a fully protected sample and several deprotected samples for different post-exposure bake times. Examples of these data are reported in Figure 5.2. Within each series, the peak widths at 1149 and 1172  $\rm cm^{-1}$  were fixed to their average value, meaning the shape could not change as a function of bake time. Typical peak widths were  $9 \text{ cm}^{-1}$ 

Wavenumber $(cm^{-1})$	Assignment
1369, 1393	CH <sub>3</sub> split umbrella mode of tert-butyl acrylate
1238	C–C–O asymmetric stretch of 4–hydroxystyrene
1255 - 1245	C–C skeletal vibrations of tert-butyl acrylate
1172	aromatic C–H in-plane bend of 4–hydroxystyrene
1149	C–O–C asymmetric stretch of tert-butyl acrylate

Table 5.1: Key IR Peak Assignments for PHOST-PTBA.

(Gaussian) and 25 cm<sup>-1</sup> (Lorentzian) at positions 1149 and 1172 cm<sup>-1</sup>, respectively, which is typical of low-density solids. The deprotection level ( $\phi$ ) is calculated from the ratio of final-to-initial TBA absorbance and corrected for changes in film thickness,

$$\phi = 1 - \frac{h_0 \left[ \text{TBA} \right]_f}{h_f \left[ \text{TBA} \right]_0},\tag{5.3}$$

where  $[\text{TBA}]_f$  is the final TBA absorbance,  $[\text{TBA}]_0$  is the initial TBA absorbance,  $h_f$  is the final film thickness, and  $h_0$  is the initial film thickness. The uncertainty (95% confidence interval) was determined by performing multiple measurements per sample, and is approximately 3% for  $\phi < 0.85$  and 5% for  $\phi > 0.85$ . The uncertainty increases at large extents-of-deprotection because the TBA signals are weak. When the deprotection level exceeds about 85%, it is difficult to distinguish the TBA signal at 1149 cm<sup>-1</sup> from the HOST signal at 1172 cm<sup>-1</sup>. However, the TBA signal at 1369 cm<sup>-1</sup> provides secondary confirmation that protecting groups are still present in the film. Note that we did not detect a change in deprotection levels based on time delay, meaning data recorded immediately after the post-exposure bake were the same as data collected after storing in a vacuum chamber for two days.



Figure 5.2: IR absorbance data for PHOST-PTBA resist with 2 wt% acid, deprotected at 70 °C. The peaks at 1369 and 1149 cm<sup>-1</sup> are associated with CH<sub>3</sub> and C-O stretches of TBA moieties, respectively.

# 5.3 Modeling Methodology.

We employed a lattice model where the material is divided into cubic elements of volume of  $1 \text{ nm}^3$ , and an acid molecule is represented by a single particle residing in one of the sites. Based on simple calculations using the density of the resin, we estimate that each lattice site contains 3 HOST and 2 TBA groups. The size of the photogenerated ions is in the range of  $0.2-0.3 \text{ nm}^3$ , which is larger than the polymer groups but smaller than the volume of each cell. The actual distances between deprotecting groups and acid molecules will depend on molecular characteristics such as an orientation [43] and fluctuations in local concentration [44]. As will become evident in the discussion, such features are implicit to our description, as we model the distribution of time intervals for acid hopping within the cubic lattice. The model assumes that reaction, escape of volatile products, and volume relaxation are all fast events, so the deprotection rates are controlled by acid mobility. Therefore, when an acid molecule jumps into a new site, this microscopic volume is instantly deprotected. The initial random distribution of acid does not deprotect any material -a hopping event must be selected prior to a deprotection event. It is important to note that allowing the acid to deprotect *before* a hopping event will produce an instantaneous deprotection level that matches the acid concentration. The difference between these initial conditions is minimal for low acid concentrations. With our chosen initial condition, deprotection profiles for a Fickian model are accelerated in proportion to acid loading. Furthermore, we avoid a situation where all acid molecules simultaneously deprotect their cells at t = 0 [51]. With regards to simulation size,  $30^3$  cells were used for the optimization scheme, while  $50^3$  cells were used to generate the final profiles.

Two different algorithms were designed to model acid hopping events on the lattice. The first algorithm uses a stochastic Kinetic Monte Carlo approach [52, 53] to reproduce a random walk described by an ergodic Markov process. Such methods are widely applied in the literature [31, 36, 54–57] and are implemented by executing reactions or displacements based on an underlying exponential distribution of time intervals associated with these events:

$$\psi(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}}.\tag{5.4}$$

For spatial displacements, Green's function for diffusion is recovered with a macroscopic diffusion coefficient D. The second algorithm employs a non-ergodic non-Markovian description based on a distribution function for waiting time intervals that follow long-tail kinetics [58] and models anomalous diffusive behavior. Such processes are increasingly observed when studying transport in complex systems, [45, 59–64] and are supported by a developing theoretical framework [65, 66]. However, to the best of our knowledge, these methods have not been employed to analyze experimental data in acid-catalyzed deprotection reactions. Additional details that pertain to the selection and implementation of this model are discussed in the Results section.
Before proceeding to the next section, we emphasize that our aim is to directly test the effects of acid diffusion on the observed macroscopic deprotection rates. Recent years have seen significant progress for characterizing diffusion in complex materials, enabled by advancements in algorithms and new experimental techniques that probe molecular length-scales [67–71]. While different waiting time distributions have been proposed in the literature, it is imperative for our work that execution is performed within a short time. This attribute allowed us to incorporate each simulation as a function evaluation within a simulated annealing optimization algorithm [72]. Each function evaluation proposes a specific value of acid diffusivity D (or  $\gamma, \tau$  depending on the model), creates a new random distribution of the acid molecules (remodeled with each evaluation), performs the simulation, and then compares the simulated deprotection profiles against experimental data. (Note that all data are projected onto the lowest acid concentration (1 wt%), which is further discussed in the Results section.) During the optimization scheme, proposed changes in the parameter D are accepted/rejected based on a Metropolis criterion at the "temperature" associated within a specific number of move attempts. We performed 20-50 runs for a specific "temperature," and by cycling through low and high temperatures, we generated a number of profiles and parameters that correspond with local minima. Each of these runs requires hundreds of function evaluations, so a simple and efficient model of anomalous diffusion [45] is absolutely essential to the success of this approach. Considering the accuracy of available data, we did not find a physical basis to introduce additional parameters apart from acid-acid interactions at high loadings (acid molecules are "phantom" particles in our model).

## 5.4 Results

We begin our discussion with an overview of macroscopic reaction kinetics. Several models for acid-catalyzed deprotection have been employed in the literature, and these examples use phenomenological parameters to describe the reaction at single phase point (temperature and acid composition). We find that a first-order reaction cannot describe our data. Furthermore, we find that acid concentration plays an important role in deprotection rates, but this behavior cannot be captured with a mesoscopic model that follows Fickian diffusion. However, deprotection profiles at different acid concentrations exhibit surprisingly similar shapes, suggesting that the same underlying mechanism controls the overall process. Using an anomalous diffusion model, we can capture the shapes of deprotection profiles for all acid concentrations and timescales. We find deviations between the model and experimental data at high acid loadings and long reaction times, and we propose that acid-acid interactions are responsible for this behavior. A simple second-order acid annihilation scheme can account for these deviations, although the underlying molecular mechanism remains unclear. Nevertheless, for all practical conditions, a simple model for acid-catalyzed deprotection based on anomalous diffusion can quantitatively describe all of our experimental data – with only two adjustable parameters.

#### 5.4.1 Macroscopic reaction kinetics

Figure 5.3a and Figure 5.3b report the deprotection level with respect to time at 70 °C. Several features that were observed in other studies are evident in our data. When the data are reported on a linear timescale (Figure 5.3a), it appears that the the reaction is self-limiting with a maximum deprotection level that depends on acid concentration [38, 73–75]. However, on a logarithmic timescale, it appears that the deprotection reaction continues with an extremely slow rate. (The increase in data



Figure 5.3: Fraction of deprotected group as a function of time in linear and logarithmic scale

scatter at long reaction times was discussed in the Experimental Methods.) Reduced deprotection rates with increasing conversion have been discussed by other studies, and this behavior is captured with phenomenological models such as volume relaxation or a temporal acid-trapping through additional reactions [37, 76]. Before we address the phenomena that control long-time behavior, we will discuss the microscopic mechanisms that control deprotection at short-to-intermediate times. We use data from resists with different acid concentrations to guide this discussion. All of our data were acquired from glassy polymer resists, meaning the deprotection temperature is well-below the polymer's glass transition ( $T_g - T \ge 50$  K). Furthermore, unless otherwise noted, the data reviewed from other studies were also based on glassy polymer resins.

The deprotection reaction is usually modeled as a first-order reaction with a very

long catalytic chain [2,31]. To quantitatively describe our data, we started with a simple analytical differential equation for reaction-limited kinetics,

$$\frac{d\phi}{dt} = k[\mathrm{H}^+](1-\phi).$$
 (5.5)

If  $[H^+]$  remains constant throughout the reaction, then the observed deprotection can be formulated with a new parameter  $K = k[H^+]$  that depends linearly on Therefore, if the acid concentration is reduced by a factor acid concentration. of 2, then the deprotection rate should be twice as slow. Some studies have reported that deprotection rate varies linearly with acid concentration [38], consistent with the model in Equation 5.5, but there are many examples where the reaction order is greater than 1. For example, Ferguson et al. reported exponents in the range of 1.2-1.8 for the deprotection of tert-butyloxycarbonyl (t-BOC) groups in poly(t-BOC-styrene sulfone) resists [73]. The range of exponents was associated with variations in temperature (always below  $T_g$ ), PAG concentration, and type of PAG. More recently, Jung et al. examined acid-catalyzed deprotection in two types of polymers: A poly(methyladamantyl methacrylate-co- $\gamma$ -butyrolactone methacrylate) (PMAdMA-PGBLMA) resin with adamantyl protecting groups, and a poly(hydroxylstyrene-co-styrene-co-tertbutyl methacrylate) (PHOST-PS-PTBMA) resin with *tert* butyl methacrylate protecting groups [77–79]. These authors measured the resist sensitivity as a function of acid loading (photospeed), which is roughly proportional to deprotection rates, and they considered reaction temperatures both below and above  $T_g$ . At temperatures below  $T_g$ , they found that halving the acid concentration would reduce the MAdMA-PGBLMA and PHOST-PS-PTBMA photospeeds by factors of 16 and 4, respectively. This result is inconsistent with first-order deprotection kinetics. In contrast, when they used laser spike annealing  $(T \gg T_g)$ , they detected first-order deprotection kinetics. To our knowledge, an increased reaction order cannot be explained by the chemistry of the deprotection reaction. Considering the data from Jung et al., it is likely that deprotection rates in polymer-based resists are controlled by the dynamical properties of the polymer resin [79].

In our experiments, we determined a macroscopic deprotection rate with a stronger-than-linear dependence on acid concentration,

$$K = k[\mathrm{H}^+]^n, \ n > 1.$$
(5.6)

The exponent n was approximately 1.6 at 70°C, 1.5 at 80°C, and 1.5 at 90°C. To demonstrate this behavior, Figure 5.3d reports all data for 70 °C on a master curve that accounts for the nonlinear dependence of reaction rate on acid concentration. For example, the data for 10 wt% PAG were multiplied by 10<sup>1.6</sup>, which superimposes those points onto the 1 wt% PAG curve. Apparently, the underlying deprotection mechanism does not vary with acid concentration, but the observed macroscopic behavior cannot be described by a simple linear rate law. Figure 5.3d also reports the model curve based on Equation 5.5 (solid black line), and this exponential decay of reacting groups does not describe the reaction kinetics. Apart from the observed slow reaction at very long times, we find a faster decrease in TBA groups at short times. Other studies of chemically-amplified resists have attributed these features to a competing thermolysis reaction [31, 76]. However, as previously discussed in the Experimental Methods, the PHOST-PTBA resin used in our studies is thermallystable [26]. With all these factors in mind, we believe a different microscopic model is needed to quantitatively describe the observed deprotection kinetics.

## 5.4.2 Fickian diffusion

The acid-catalyzed deprotection of glassy polymer films has been studied for more than 30 years. While it is widely accepted that acid diffusion controls the macroscopic reaction rate, models based on Fickian diffusion cannot adequately describe experimental data [80,81]. Instead, various phenomenological diffusion models were proposed that reduce the acid transport rates with increasing extent-ofdeprotection. This view is supported by many studies of acid transport in deprotected and protected polymers, where extremely low diffusivity in the deprotection phase  $(10^{-16}-10^{-18} \text{ cm}^2/\text{s})$  is orders of magnitude less than the protected phase  $(10^{-12}-10^{-18} \text{ cm}^2/\text{s})$  $10^{-14}$  cm<sup>2</sup>/s) [31, 33, 82]. One such model suggests that volatile reaction products create additional free volume, which subsequently decays to an equilibrium state as these molecules desorb and the polymer relaxes [37]. While this scenario is plausible, the model introduces several parameters that are difficult to estimate or measure. Furthermore, some experiments suggest that desorption is much faster than deprotection, which is in direct contrast to the volume-relaxation mechanism [83]. Other efforts propose a simple relationship between acid diffusivity and extent-of-reaction, such as a linear *increase* in diffusion rate with increasing deprotection level [39, 41]. While this view is not supported by direct measurement of acid transport, such models can describe the image blur in a real photoresist. Considering the difficulties in determining an appropriate acid transport model, experimental data are often interpreted with Fickian diffusion using a constant acid diffusivity [35,75,84]. In summary, models for acid-catalyzed deprotection face significant challenges in capturing both short-time and long-time behavior. Therefore, depending on the aim of each study, different parameters are introduced to capture the timescale of interest.

Stochastic simulations have been used to describe reaction kinetics and acid



Figure 5.4: Fickian diffusion model

transport in chemically-amplified resists [31, 36, 55–57, 85]. Using a lattice Kinetic Monte Carlo algorithm [52–54], we defined a microscopic model based on an explicit description of acid molecules that perform random walks with Gaussian statistics. Following the description in the Modeling Methods section, the only adjustable parameter within the simulated annealing scheme was the diffusion coefficient D. For this refinement of D, we used the master curve described in Figure 5.3d rather than the individual data sets, which improves the algorithm's reliability and the speed of simulations. After extracting the diffusivity D for low acid concentration (1 wt%), we independently created profiles for higher acid loadings using the same D. Table 5.2 reports the values of D as a function of temperature, and Figure 5.4 plots the

Model Temperature	$70^{\circ}\mathrm{C}$	80°C	90°C
$Fickian \ diffusion \ D \ ({ m cm}^2/{ m sec})$	$8.4 \times 10^{-18}$	$5.5 \times 10^{-17}$	$3.9 \times 10^{-16}$
Anomalous diffusion au (sec) $\gamma$	$4.1 \times 10^{-1}$ 0.44	$7.6 \times 10^{-2}$ 0.46	$2.3 \times 10^{-2}$ 0.47
Anomalous diffusion with annihilation $\tau$ (sec) $\gamma$	$7.8 \times 10^{-1}$ 0.53	$2.1 \times 10^{-1}$ 0.59	$6.6 \times 10^{-2}$ 0.67

Table 5.2: Parameters extracted for the two different models

simulated deprotection level for Fickian diffusion against the experimental data. The extracted values of D are consistent with other reports of acid mobility in deprotected resins [2].

Two aspects of the simulations merit further discussion. Referring to Figure 5.4, we observe that the simulated curve is an exponential growth – much like the analytical model described by 5.5 and reported in Figure 5.3. Furthermore, the simulated deprotection rate has a linear dependence on acid concentration. The apparent first-order dependence on acid concentration is a consequence of independent random walks, where the mean-square displacement of acid molecules grows linearly with time, reproducing a Fickian diffusion coefficient as shown in Figure 5.4d. In summary, while the simulated profiles can capture the correct time scale for deprotection, they do not provide quantitative agreement with experimental data.

#### 5.4.3 Anomalous diffusion

As discussed earlier, a simple microscopic Fickian diffusion mechanism fails to capture the macroscopic deprotection rate. However, this discrepancy could be associated with an underlying hopping process that presents features of anomalous diffusion [45, 59, 61–64]. At first glance, the deviations from Fickian diffusion seem consistent with acid-anion hopping described by a waiting time distribution with longtail kinetics [58]. Such dynamic processes exhibit a stretched exponential behavior that is reminiscent of probe diffusion in polymer glasses [67, 86–88]. Several models have been proposed that provide a quantitative description of anomalous diffusion in complex materials [62, 68–70, 89]. For our studies, we chose the mathematical formalism of a continuous random walk, where sub-diffusive behavior originates from acid hopping described by a broad distribution of waiting times [45, 90]. Waiting times were selected from the Pareto distribution [66],

$$\psi(t) = \frac{\gamma/\tau}{(1+t/\tau)^{(1+\gamma)}},$$
(5.7)

where  $\gamma$  is the anomalous exponent and  $\tau$  is the characteristic time. This probability density function allows rapid sampling of waiting times between successive hopping processes, and has the required long-time asymptotic scaling [59, 60, 66],

$$\psi(t) \propto \frac{\gamma}{\tau} \left(\frac{t}{\tau}\right)^{-1-\gamma}.$$
(5.8)

The algorithm was implemented as described in the literature, with instantaneous reaction when an acid translates to a non-deprotected lattice site [51, 66]. Kinetics are controlled solely by acid transport, which is described with only two parameters,  $\tau$  and  $\gamma$ . We proceeded by determining these parameters for the lowest acid concentration at each temperature, and then we predicted the profiles for the remaining acid concentrations. Figure 5.5 provides significant insight into the microscopic mechanism of the reaction process. For low concentrations and short times, the model of anomalous diffusion offers a quantitative description of bulk deprotection



Figure 5.5: Anomalous diffusion model

data that is consistent with the observed dependence on acid concentration. The underlying feature that generates this macroscopic behavior is the subdiffusive character of acid transport, where the mean-square displacement is

$$<\Delta r^2(t)>_{\rm ens} \propto t^{\gamma}.$$
 (5.9)

This subdiffusive behavior is depicted in Figure 5.5d with  $\gamma < 1$ . Extraction of these data requires ensemble averaging without time averaging; the latter could produce inhomogeneous Fickian diffusion [91]. The subdiffusive model has a diffusion coefficient that depends on time. However, a constant value can defined with the use of

fractional derivatives [45]. Within the fractional derivative description, we extract a diffusion coefficient  $D_{\gamma}$  with values of  $3.0 \times 10^{-15}$ ,  $5.8 \times 10^{-15}$ , and  $5.3 \times 10^{-14} \text{ cm}^2/\text{sec}$ for 70 °C, 80 °C and 90 °C, respectively [66,92]. Note that long-tail kinetics lead to higher values of D, which is similar to findings based on Fickian diffusion with an acidtrapping process [75]. Nevertheless, as we show in the next section, an irreversible trapping reaction within a local volume cannot capture the higher-order dependence on acid loading. Within the subdiffusive framework, the acid molecules experience short-time displacements, but long-range diffusion is significantly penalized. These characteristics are needed to capture the experimental data in our studies, and other works have also emphasized the same points - models must include short-range fast dynamics while accounting for the extremely low diffusion coefficient in the deprotected polymer [33]. Clearly, the chemistry involved in the reaction-diffusion process is quite complex and not fully understood. However, the subdiffusive model provides a unique insight into the underlying physics, and offers a good description of the process with only two free parameters. Furthermore, the concept is consistent with other studies of inert probe diffusion in glasses [67,86–88].

## 5.4.4 Acid-acid interactions

The microscopic view of subdiffusive transport is consistent with experimental data for low acid concentrations and short reaction times. However, at higher acid loadings and longer reaction times, the subdiffusive model over predicts the extent-ofdeprotection. (In contrast, Fickian diffusion under-estimated the deprotection level at short-times for all acid loadings.) While industrial processes tend to focus on lower acid loadings and short deprotection times, we sought to identify the cause of such deviations.

Acid loss will reduce the deprotection level at long times. We attempted to



Figure 5.6: (a) Anomalous diffusion model with a linear acid loss  $dH^+/dt = -k[H]$  with  $\tau = 0.26$  sec,  $\gamma = 0.44$  and  $k = 5.5 \times 10^{-5}$  molecule/sec. (b) - (d) Anomalous diffusion model with partial deactivation upon acid-acid encounters.

annihilate a selected acid molecule based on an additional rate in-between hopping intervals [65,66], which is similar to phenomenological acid-trapping models proposed in other works [35,38,74,75,84]. This mechanism provides a quantitative description of the deprotection rates at low acid loadings (1 wt%), but cannot capture the data for higher acid loadings with the same values for  $\tau$ ,  $\gamma$ , and trapping rate. Specifically, we observe significant deviations between predicted and measured profiles at short times. These results are included in Figure 5.6a. To describe our data, the loss mechanism must depend on acid concentration in addition to time. Our model employs a simplistic picture of acid molecules that translate as "ghost" particles without any explicit interactions. This assumption could break down when these large ionic molecules are within a volume of 1 nm<sup>3</sup>. Furthermore, reaction products could be present within their immediate environment, and it is unclear how the local composition impacts the reaction chemistry. Therefore, we proposed a simple loss mechanism that does not require specification of new parameters: An acid molecule is deactivated if it hops into an already occupied lattice site, which is equivalent to the following instantaneous annihilation process,

$$\mathrm{H}^{+} + \mathrm{H}^{+} \to \mathrm{H}^{+}. \tag{5.10}$$

This process occurs when acid molecules are within 1 nm of each other, which is equal to the lattice grid and an implicit feature of the algorithm. Using this simple approach, we can quantitatively describe all data at 1, 2 and 4 wt% acid loading with two parameters for the distribution of waiting times. Results are summarized in Figure 5.6. Small deviations persist for the 10 wt% loading, but this may be associated with the initial conditions: At such high concentrations, it is possible that the spatial distribution of the PAG is not uniform [55], or perhaps there is a plasticizing effect that leads to faster deprotection rates at the highest temperatures [93]. Two data sets for 90 °C exhibit a plateau at long times (ca. 1-10 hours) that is not captured by the acid depletion model, and the reason for this behavior is unknown. Similar trends have been observed in other studies that incorporate a base quencher [2,94]. While our resist formula does not contain base additives, it is possible that airborne contaminants were slowly adsorbed onto the surface of these films, accidentally deactivating the catalyst with a very slow timescale. The origin of the phenomenological acid depletion is unclear. The reaction proposed by Equation 5.10 may capture aggregation (with collective movement of aggregates) [30], or an increased local acid concentration may shift the reaction equilibrium to render the catalyst partially inactive [2]. Currently, we do not have direct measurements that support any of these mechanisms. However, most of the catalyst is ultimately deactivated by this model, and aggregation alone cannot explain this behavior - there is no evidence of large-scale phase separation in microscopy measurements of the resists films.

To highlight the differences between a Fickian diffusion model and subdiffusive behavior, we modeled a system with a very low initial concentration of acid (0.05 wt%) to facilitate visualization of the process. Note that acid-acid interactions are not relevant in this case. The evolution of this system at 80 °C is illustrated in Figure 5.7, where simulations were based on the best-fit parameters for Fickian and anomalous diffusion (with annihilation) as reported in Table 5.2. Within 10 min, the anomalous diffusion model predicts 3% (volume) of reacted material, while the Fickian model predicts 1%. After two hours, almost 11% of the material has undergone deprotection with either model. After 24 hours, the Fickian and anomalous transport models predict 70% and 32% conversion, respectively.



Figure 5.7: Snapshots of a 0.05 wt% acid system at  $80^{\circ}$  for the Fickian model (F) and anomalous diffusion with acid-acid interactions (A). Parameters are summarized in 5.2. Initial acid positions are rendered with the red particles, and reacted material is represented by white particles.

## Chapter 6 Sample Preparation

This chapter describes the underlying steps in the preparation of nanopatterned samples process, from the substrate preparation, nanofabrication to post processing. Thickness uniformity of the spun cast films was an important criteria in sample preparation. This chapter also includes a discussion on the optimization of each step of the process.

# 6.1 Sample Preparation Process

## 6.1.1 Substrate Preparation

Transmission SAXD experiments require the substrate to be transparent, therefore all samples were fabricated on silicon nitride (SiN) membranes. Silicon wafers with 100 nm thick low stress SiN on both sides was purchased from University Wafer. One side of each wafer was patterned with an array of windows using photolithography with S1813 resist. The SiN film was removed from the patterned windows using CHF<sub>3</sub> reactive ion etch. The membranes are created in these windows by etching away the silicon using a 30 wt% potassium hydroxide aqueous solution at 57°C for 12 hours. The etched membranes span 1350  $\mu$ m x 750  $\mu$ m. These membranes were soaked in de-ionized water (DI) for 24 hrs., rinsed in 0.1N Hydrochloric acid 5 min. and DI water, dried in Nitrogen gas stream prior to storage.

The substrates were cleaned with Piranha solution (three parts sulfuric acid, one part 30 wt% aqueous hydrogen peroxide) for 15 minutes which destroys any organic contamination and gives an extremely hydrophilic surface followed by a DI wash. The substrates were then dehydration baked at 130°C for 5 minutes prior to spin casting.

Due to the sensitive nature of the chemically amplified resist systems, the substrate preparation and cleaning procedure plays a key role in the success of the image formation process. It is observed that insufficient cleaning after the wet etch process of the membranes can affect the acid generation at exposure.

### 6.1.2 Processing Steps

The sample preparation process is illustrated below:



Figure 6.1: Sample preparation process.

## Spin Casting and Post Apply Bake

A 80 nm thick film was spun cast on a silicon nitride membrane, by taping the chip on a silicon wafer. Details of this step is discussed in Section 6.2. The sample was then post apply baked (PAB) at 130°C for 2 mins. The PAB step ensures the solvent evaporation from the spun cast film by heating the sample to near its glass transition temperature. The "bulk"  $T_g$  of the polymer is reported to be 140°C [1].

## Nanopatterning

Nanopatterning generates the acid in the CAR system. Electron beam lithography based on a scanning electron microscope equipped with Nano Pattern Generation Software (NPGS) was used to irradiate the above prepared films. The patterns consist of line gratings of 20 $\mu$ m length and 170 nm pitch, single pass with a specified line width of 1.37 nm. The gratings were patterned using a 2000x magnification with a field size of 90  $\mu$ m x 90  $\mu$ m. The overall patterned area was 500  $\mu$ m x 500  $\mu$ m located at the center of the membrane (Figure 6.2). Four samples were patterned at each patterning cycle to ensure consistency.



Figure 6.2: Nano-line grating patterned using NPGS software at the center of the membrane.

### Post Exposure Bake (PEB)

For our experiments we measured the temperature dependance of the latent image formation. The process parameters were PEB temperature and time,  $90^{\circ}$  - 140°C and 10, 15 and 20 sec. At each cycle, three samples were PEB at a given temperature for the above times while one sample was developed to ensure the process integrity.

Figure 6.3 illustrates the AFM images of the latent images of the nanoline gratings at the lowest PEB temperature. The volume loss due to deprotection can be seen as approx. 3 nm surface bumps, where the surface dips indicate the deprotected regions. At these PEB times it was not expected to see a trend in volume loss, due to the instantaneous reaction kinetics. However, the three samples were used for verification purposes.



Figure 6.3: AFM micrographs of the latent image of a 170 nm pitch line grating PEB for (a) 10 sec (b) 15 sec (c) 20 sec at  $90^{\circ}$ C.

## Development

Development dissolves the deprotected polymer thus leaving the protected areas behind. Analysis of the developed image reveal the effectiveness and approximate dimensions of the patterns. However the dissolution process introduces additional factors into the analysis. We developed one film from each patterning cycle after PEB in 0.062N tetramethylammonium hydroxide (TMAH) solution for 25 sec followed with a DI rinse for 10 sec. Figure 6.4 illustrates a AFM micrograph of a developed nanoline grating.



Figure 6.4: AFM micrograph of the relief image of a 170 nm pitch line grating PEB for 20 sec at  $90^{\circ}$ C and developed in 0.062N TMAH for 25 sec.

## 6.2 Process Variables

In summary, the process variables associated with the experiment are illustrated in Table 13.3 below:

The parameters of interest for this study are, Post Exposure Bake temperature and Post Exposure Bake time. The remaining parameters, as explained below were optimized for the system.

Solution	Spin cast-	PAB	EBL	PEB	Development
prep.	ing				
Polymer	Film thick-	Temp.	Voltage	Temp.	Conc.
conc.	ness				
Photoacid		Time	Current	Time	Time
conc.					
Base conc.			Grating		
			pitch		
			Dose		

Table 6.1: The variables that describe the system

#### 6.2.1 Solution Preparation

The resist formula consist of 4 wt.% copolymer and 4 wt.% PAG in PGMEA solvent. The polymer concentration was chosen to yield a 80 nm thick film.

### 6.2.2 Film Thickness

For our experiments, having a very uniform film on the membrane was extremely critical. Non-uniform films may affect the catalyst diffusion as well as introduces complexity in modeling the x-ray data. Therefore several techniques were investigated to enhance the uniformity of the film across the silicon nitride membrane.

We explored the possibility of coating the back of the wafers with a thin film of thermally conductive metal to aid in spin casting uniformity. Thermally conductive substrates, such as silicon, aluminum and copper produce very flat thin films when resist spun on them. However, when the substrate is an insulating membrane embedded in a thermally conductive material there could be variations in film thickness due to variations in evaporation rate. In order to investigate this we used different substrates and different methods of spin casting on membranes. Topography of the films were analyzed using microscopic techniques.

It can be seen from the Figure 6.5 and Figure 6.6 that a 100 nm Aluminum



Figure 6.5: 100 nm thick silicon nitride membrane backed with 100 nm evaporated copper: (a) bare membrane (b) resist film spun by taping the chip on a silicon wafer (c) film spun using a plastic spin chuck.

film evaporated at the back of the membranes did not contribute much towards the uniformity of the film. Since the metal evaporation process introduces two additional processing steps of evaporation before spin casting and removal of the metal from the substrate prior to x-ray measurements, this process was omitted from further consideration.

Another option was the use of a thick membrane. To evaluate this a resist film was spun of a 500 nm thick silicon nitride membrane (Figure 6.7). However, the 20.5 nm thickness variation observed was higher for the thicker nitride membrane.



Figure 6.6: 100 nm thick silicon nitride membrane backed with 120 nm evaporated aluminum: (a) bare membrane (b) resist film spun by taping the chip on a silicon wafer (c) film spun using a plastic spin chuck.



Figure 6.7: 500 nm thick silicon nitride membrane without metal evaporation: (a) bare membrane (b) resist film spun by taping the chip on a silicon wafer. Attempts using a poly(tetrafluoroethylene) spin chuck with 4 metal pins to secure the chip result in a gradient in film thickness across the membrane. Taping the chip on a silicon wafer using double-sided tape produced better results, but this method result in two regions on the membrane where the film was much thicker than the rest. However by adjusting the distance between the center of the wafer and the center of the membrane we were able to obtain a reasonably uniform film at the center of the membrane (Figure 6.8 and Figure 6.10). The calculated thickness variation of the membrane was 4.98 nm compared to 3.51 nm on a silicon wafer (Figure 6.9).



Figure 6.8: Resist films spun cast on 100 nm thick bare silicon nitride membranes by taping them on a silicon wafer and spinning on a vacuum chuck. Depending on the position of the chip on the wafer the uniformity varies. Position B and C shows better results.



Figure 6.9: (a) AFM image of the resist film surface of a film spun cast on a silicon wafer (b) AFM surface image of a film spun on a silicon nitride membrane using a plastick spin chuck.



Figure 6.10: AFM images of the resist film spun on Position B 6.8 above: (a) edge of the membrane (b) between the middle and the edge of the membrane (c) middle of the membrane.

An effort to use solvent annealing as a means to improve the topography did not produce significant results when annealed to 20 minutes. However due to contamination issues the once spun on the substrate the films cannot be kept longer in atmospheric conditions, thus was not a good alternative.

### 6.2.3 Post Apply Bake

To determine the best PAB conditions we spun cast 80 nm copolymer films (no acid) on clean silicon substrates, measured film thickness before and after annealing in a shielded hotplate at 120 - 180°C for 60 and 120 sec (Figure 6.11). It could be observed that above 140°C, the volume loss increases, possibly due to small levels of thermally induced deprotection. PAB condition at 130°C for 120 sec was chosen to be the best.



Figure 6.11: Optimization of post apply bake temperature: film thickness loss increases with increasing bake temperature.

## Chapter 7 Patterning: Lithography

This chapter illustrates the lithographic processes followed in our experiments. Projection lithography is being industrially used in nanopatterning chemically amplified resists while Electron beam lithography being popular in the research community. Our samples were nanopatterned with an electron beam system consist of a scanning electron microscope equipped with a pattern generation system, which is discussed in this Chapter.

## 7.1 Electron Beam Lithography (EBL)

Patterning with electrons is accomplished by focusing a very narrow beam of electrons onto the resist. Electrons have potential to very high resolution, due to the fact that the wavelength of electrons being very small, thus electron diffraction occurs over atomic distances [95]. The calculated wavelength of electrons with an energy of 30 keV by de Broglie wavelength equation is 0.0071 nm. Electron beams are deflected electromagnetically, therefore they can be moved at very high speeds. The beam spot is scanned according to the user specified shapes of patterns. Thus, EBL is a pointby-point direct write technique which has the disadvantage of being much slower than the photolithography techniques. EBL is mainly used for photomask production and device prototyping.

The pattern is written by adopting a vector scan method (Figure 7.1), by which only the pattern writing area is scanned with the electron beam. Several factors determine the resolution of an EBL system such as the size of the source, column demagnification, spherical aberrations of the lenses as well as the electron wavelength which can limit the beam diameter by diffraction effects at very high resolutions. In addition factors such as resist chemistry and proximity effects also contribute towards resolution.



Figure 7.1: Vector scan process in electron beam lithography.

#### 7.1.1 Principle

A typical EBL column consists of the source, lenses, a mechanism to deflect the beam, a beam blanker and an electron detector for assisting with focusing and imaging (Figure 7.2). For our experiments a Philips XL30 FEG scanning electron microscope (SEM) equipped with a Nano Pattern Generation System (NPGS) software was used. The electron source was a Schottky-based thermionic emission type, in which the electrons escape over the work function barrier by way of thermal excitation. Schottky emitters consist of a tungsten tip coated with zirconium oxide which has the ability of increasing the electrical conductivity at high temperature. The generated electrons are focused by magnetic forces : two circularly symmetric iron polepieces with in between copper winding creates the magnetic lenses. The divergence of the magnetic flux along the optical axis imparts a force on electrons towards the optical axis, resulting in beam focusing.

The size of the beam can be controlled using apertures, which are small holes through which the beam passes on its way. A blanking aperture can be used to turn the beam on and off, by deflecting the beam away from the aperture hole so that the aperture intercepts the beam when not writing. A beam limiting aperture sets



Figure 7.2: Electron beam lithograpy.

the beam convergence angle thus controlling the effects of lens aberrations and thus the resolution, and also sets the beam current. In our EBL system, the absence of a beam blanking aperture is compensated by the NPGS software [96], which directs the beam away from the aperture hole when not writing on the pattern.

The SEM-EBL system does not include a dynamic focus correction mechanism, therefore a manual focus correction procedure was followed each time a sample was patterned. In order to verify the focus correction process, different areas of the nanopattern were imaged and compared using Atomic Force Microscopy.

## 7.2 Electron-Solid Interactions

Resolution limit of an electron beam lithography system can be theoretically described by the diffraction of electrons. For Gaussian beam system the beam diameter d is defined by [97],

$$d^{2} = \left[\frac{i}{B} + (1.22\lambda)^{2}\right]\frac{1}{\alpha^{2}} + (0.5C_{s})^{2}\alpha^{6} + \left(\frac{\Delta E}{E_{0}}C_{c}\right)^{2}\alpha^{2},$$
(7.1)

where *i* is a beam current, *B* is a brightens of an electron source,  $\alpha$  is the convergence half-angle of an electron beam,  $C_s$ ,  $C_c$  are the spherical and chromatic aberration coefficients of the final lens, and  $E_0$  and  $\Delta E$  are the average energy and the energy spread of the electrons in the beam accordingly. However, as the electron beam approaches the resist film, the resulting electron-solid interactions result in deviation of the beam shape from the theoretical approximation.

As electron penetrate the resist, several scattering events are observed (Figure 7.3). Forward scattering, which tend to broaden the initial beam diameter. The majority of the electrons penetrate the substrate are back scattered. The above phenomena leads to proximity effect.



Figure 7.3: Electrons-solid interactions: forward scattering and back scattering.

#### 7.2.1 Forward Scattering

Some of the electrons penetrating into the resist undergo small angle scattering events, which can significantly broaden the beam profile through the depth of the film. It is empirically determined that the increase in effective beam diameter due to forward scattering can be calculated by the formula  $d_f = 0.9 (R_t/V_b)^{1.5}$  [98], where  $R_t$  is the resist thickness in nm and  $V_b$  is the beam voltage in kV. Reduction in film thickness and increase in the beam accelerating voltage would minimize forward scattering.

### 7.2.2 Secondary electrons

As the primary electrons are slowed down, much of their energy is dissipated as secondary electrons. Much of the exposure process is done by the secondary electrons. The movement of the secondary electrons range only a few nanometers. Therefore their contribution to proximity effect is very less, but can cause beam widening.

## 7.2.3 Backscattering

Many of the electrons that penetrate through the resist into the substrate experience wide angle scattering events, due to collisions with heavy particles such as nucleus. These electrons may return back through the resist resulting in additional exposure. The extent of backscattering depends on the substrate and less dependant of the beam energy.

## 7.2.4 Proximity effect

Proximity is the phenomena of the exposure dose distribution being wider than the scanned image. The key contributor to this phenomena is back scattering [99]. The effect can be approximated by a double Gaussian model. A point-like electron beam is broadened to a superposition of a gaussian with a width of  $\alpha$  due to forward scattering and a gaussian with a width  $\beta$  due to backscattering can be described by

$$f(r) = \frac{1}{\pi (1+\eta)} \left[ \frac{1}{\alpha^2} \exp(\frac{-r^2}{\alpha^2}) + \frac{\eta}{\beta^2} \exp(\frac{-r^2}{\beta^2}) \right].$$
(7.2)

Where  $\eta$  is the ratio of the backscattered energy to the forward scattered energy. Thus the final exposing energy incident on the resist can be obtained by combining the exposed pattern and the proximity function as:

$$E(r) = Q K \left[ \left(\frac{1}{\sigma_{f}}\right)^{2} \exp\left(\frac{-r^{2}}{\sigma_{f}^{2}}\right) + \left(\frac{\eta}{\sigma_{b}^{2}}\right) \exp\left(\frac{-r^{2}}{\sigma_{b}^{2}}\right) \right].$$
(7.3)



Figure 7.4: Optical and AFM micrographs proximity effect on a silicon substrate.

Proximity effect can be minimized in several ways. One is to adjust the exposure dose of a uniform pattern till the desired linewidth is attained. Higher beam energy minimized the forward scattering while averaging the backscattering over a larger area. We used a beam energy of 30 keV, which was the maximum limit of the instrument, and the smallest available beam spot size (beam diameter) for nanopatterning. In addition, since backscattering depends on the substrate material, replacing the high atomic number material with low atomic number materials enable minimizing the backscatter [100]. Figure 7.4 illustrates an outcome of proximity effect of 190 nm line grating of CA resist on a silicon substrate. Therefore, to minimize the effects of backscattering our nanopatterns were positioned on 100 nm thick silicon nitride membranes. Further, the graphite placed underneath absorbs the transmitted beam.

# 7.3 Speed

The point by point exposure in electron beam lithography makes the process much slower compared to optical lithography technique where mass production is possible. The time takes to generate a pattern depends on the dose (C/cm<sup>2</sup>), beam current (A), the pattern area (cm<sup>2</sup>),

$$Dose = \frac{Current X Exposure time}{Pattern area}.$$
 (7.4)

The scanning speed, F (Hz) is a function of the scan step size (cm),

$$F = \frac{\text{Current}}{\text{Dose X Step size}^2}.$$
(7.5)

# 7.4 Optimum Exposure Conditions

The sensitivity of the CA resists may result in "amplification" due to minute changes to the composition of the resist system, making the optimum exposure conditions vary. Therefore, the optimum exposure conditions were calibrated each time a new resist solution is prepared.

For a given resist composition, a test sample was prepared spin casting a 80 nm thick film followed by post apply bake for 2 mins at  $130^{\circ}$ C. A set of 90  $\mu$ m x 90  $\mu$ m areas was patterned with line gratings of 170 nm grating pitch, 20  $\mu$ m length and 1.37 nm line width, each 90  $\mu$ m x 90  $\mu$ m field having a single dose. The exposure dose was varied over a wide range with 5% increments of the original dose. The sample was then post exposure baked (PEB) for 20 secs at 130°C, which was used as the calibration PEB condition, and developed.

The region exposed at optimum conditions was determined using optical microscopy and AFM. Optical microscopy reveals the uniformity of dissolution in a macroscopic scale, which can be used as the preliminary screening. A combination of high and low resolution AFM micrographs can provide information on the level of dissolution. At a 170 nm pitch, it is difficult for a standard cantilever to reach the entire height of the nanolines. However we have observed that at 100% dissolution, the depth of penetration of the cantilever is 20 - 25 nm (Figure 7.5). The optimal exposure conditions for the example illustrated in Figure 7.5 below was 0.38 nC/cm. The cross section profile of 0.42 nC/cm indicates that at that dose most of the film has been washed away resulting the height of the nanolines being shorter than the overall film thickness of 80 nm.



Figure 7.5: Calibration
# Chapter 8 X-ray Reflectivity

X-ray reflectivity is a surface sensitive technique based on the principle that for x-ray wavelengths where  $\lambda \sim 1$ , the refractive index being smaller than unity. This technique recognizes the different refractive indices of each layer in a multilayer system. The two mathematical approaches for data analysis are Abeles matrix method and Parratt recursive technique. We employ Parratt recursive method in our analysis, which is detailed in this Chapter. The volume loss due to deprotection in CA resists increases the density of the deprotected polymer which we expected would produce x-ray scattering contrast. Analysis of x-ray reflectivity data produces the scattering length density of the polymer which is directly proportional to its electron density. Therefore, the analysis of the reflectivity data not only served as a feasibility study, but also generated a direct input parameter to model the small angle scattering data.

# 8.1 Principle

When an electromagnetic plane wave of which the electric field vector  $E(\mathbf{r}) = \mathbf{E}_{o} \exp(i\mathbf{k}_{i} \cdot \mathbf{r})$  penetrates into a medium with a refractive index of  $n(\mathbf{r})$ , it propagates according to the Helmholtz equation,

$$\Delta \mathbf{E}(\mathbf{r}) + \mathbf{k}^2 \mathbf{n}^2(\mathbf{r}) \mathbf{E}(\mathbf{r}) = 0.$$
(8.1)

Note that the modulus of the wave vector is  $\mathbf{k} = 2\pi/\lambda$  where  $\lambda$  is the x-ray wavelength.

Refractive index of a medium consist of N atoms per unit volume can be assumed to be harmonic oscillators with resonance frequencies  $\omega_{j}$ :

$$n^{2}(\mathbf{r}) = 1 + N \frac{e^{2}}{\varepsilon_{o}m} \Sigma_{j=1}^{N} \frac{f_{j}}{\omega_{j}^{2} - \omega^{2} - 2i\omega\eta_{j}}, \qquad (8.2)$$

where  $\omega$  is the frequency of the incoming wave, e and m are the charge and the mass

of an electron,  $\eta_j$  are the damping factors and  $f_j$  are the forced oscillation strengths of the electrons. For x-rays of  $\omega > \omega_j$  this can be simplified to

$$\mathbf{n}(\mathbf{r}) = 1 - \delta(\mathbf{r}) + \mathbf{i}\beta(\mathbf{r}), \qquad (8.3)$$

where,

$$\delta(\mathbf{r}) = \frac{\lambda^2}{2\pi} \mathbf{r}_{\mathbf{e}} \varrho(\mathbf{r}) \Sigma_{\mathbf{j}=1}^{\mathbf{N}} \frac{\mathbf{f}_{\mathbf{j}}^{\mathbf{o}} + \mathbf{f}_{\mathbf{j}}'(\mathbf{E})}{\mathbf{Z}}, \qquad (8.4)$$

$$\beta(\mathbf{r}) = \frac{\lambda^2}{2\pi} \mathbf{r}_{\mathbf{e}} \varrho(\mathbf{r}) \Sigma_{\mathbf{j}=1}^{\mathbf{N}} \frac{\mathbf{f}_{\mathbf{j}}''(\mathbf{E})}{\mathbf{Z}} = \frac{\lambda}{4\pi} \mu(\mathbf{r}), \qquad (8.5)$$

with the classical electron radius  $r_e$ , total number of electrons  $Z = \Sigma_j Z_j$ ,  $Z_j$  being the number of electrons of each component of the material, the linear absorption coefficient  $\mu(r)$  and and the electron density  $\rho(r)$  as a function of the spatial coordinates r = (x,y,z).

 $\delta(\mathbf{r})$  is always positive. The quantities  $f_j^o$  depends on  $\mathbf{q}$ , which is the wavevector transfer.  $f_j^o$  becomes significant with a large  $\mathbf{q}$ -region, however in gracing incident and exit angles where  $\mathbf{q}$  is small  $f_j^o$  can be approximated by  $Z_j$ .

For a homogeneous medium Equation 8.3 can therefore be expressed as,

$$n = 1 - (\lambda^2/2\pi)r_e\varrho + i(\lambda/4\pi)\mu.$$
(8.6)

#### 8.1.1 Reflection from a single interface

Assume a perfectly smooth vacuum/medium interface. The incoming plane wave (Figure 8.1), the reflected and the transmitted fields can be described using the law



Figure 8.1: A plane electromagnetic wave interacts with a medium at gracing incidence. The wave is partially reflected and partially transmitted.

of refraction as:

$$\mathbf{k}_{\mathbf{i}} = \mathbf{k} \left( \cos \alpha_{\mathbf{i}}, 0, -\sin \alpha_{\mathbf{i}} \right), \tag{8.7}$$

$$\mathbf{k}_{\mathbf{f}} = \mathbf{k} \left( \cos \alpha_{\mathbf{i}}, 0, \sin \alpha_{\mathbf{i}} \right), \tag{8.8}$$

$$k_t = (k_{t,x}, 0, k_{t,z}).$$
 (8.9)

If the case where the incoming wave is linearly polarized in the y-direction (plane perpendicular to the scattering plane x-z, s-polarization) is considered, since the electric and the magnetic fields have to be continuous at z=0, the reflected ( $r_s$ ) and the transmitted ( $t_s$ ) components can be expressed by the Fresnel formulas:

$$\mathbf{r}_{s} = \frac{\mathbf{k}_{i,z} - \mathbf{k}_{t,z}}{\mathbf{k}_{i,z} + \mathbf{k}_{t,z}}, \qquad (8.10)$$

$$t_s = \frac{2k_{i,z}}{k_{i,z} + k_{t,z}},$$
 (8.11)

where  $k_{i,z} = k \sin \alpha_i$  and  $k_{t,z} = nk \sin \alpha_t = k (n^2 - \cos^2 \alpha_i)^{1/2}$ . It can ne shown that since n is almost unity for x-rays, practically the same result could be obtained for the p-polarized waves as well. Henceforth the transmitted and the reflected components will be denoted as 't' and 'r' respectively.

The Fresnel reflectivity in the small angle regime,  $R_{\rm F} = |r|^2$  would be

$$R_{\rm F} = \frac{(\alpha_{\rm i} - p_{+})^2 + p_{-}^2}{(\alpha_{\rm i} + p_{+})^2 + p_{-}^2}, \qquad (8.12)$$

$$p_{+/-}^2 = \frac{1}{2} \{ \sqrt{(\alpha_i^2 - \alpha_c^2)^2 + 4\beta^2} \pm (\alpha_i^2 - \alpha_c^2) \}, \qquad (8.13)$$

where  $p_{+/-}^2$  being the real an imaginary part of the complex transmission angle  $\alpha_t = p_+ + ip_-$ .

For a vacuum-medium interface from the law of refraction,  $\cos\alpha_i = (1 - \delta) \cos\alpha_t$ with  $\alpha_t$  being the exit angle of the refracted wave. If  $\alpha_t = 0$ , since  $\delta$  is small, the critical angle can be defined as,  $\alpha_c \approx \sqrt{2\delta} = \lambda \sqrt{r_e \rho / \pi}$ . The depth of penetration of the x-ray wave at gracing angles  $\alpha_i \to 0$  is approximately,  $\Lambda_0 = \lambda / (2\pi\alpha_c) = 1/\sqrt{4\pi r_e \rho}$ . Therefore the depth of penetration is independent of the wavelength  $\lambda$ .

Total reflection occurs for incident angles  $\alpha_i \leq \alpha_c$ : x-rays do not penetrate far into the medium, but all incoming radiation is reflected. For  $\alpha_i > \alpha_c$ , the penetration depth  $\Lambda$  increases rapidly, and only limited by the absorption of the material.

#### 8.1.2 Reflection from Sharp Multiple Interfaces

For simplicity, scattering from several sharp interfaces is considered (Figure 8.2). The incoming wave with a unit amplitude impinges on the vacuum-layer 1 interface at an incident angle of  $\alpha_i$ . As discussed in the previous section, portion of the incoming wave is reflected while the rest being transmitted. The transmitted wave becomes the incoming wave at the successive interface and the process continues up to the



Figure 8.2: Reflection from N interfaces. The incident wave amplitude is normalized to unity, T1 = 1.

layer N-substrate interface at which the transmitted portion gets absorbed due to the high absorptivity of the substrate.  $T_j$  and  $R_j$  are the amplitudes of the transmitted and reflected waves respectively. Refractive index of layer j, is  $n_j = 1\delta + i\beta$  and the thickness is  $d_j = z_{j-1} - z_j$ . The transmitted and the reflected wavevectors are  $k_{i,j}$  and  $k_{f,j}$ .

Parratt (1954) introduced a recursive approach to reflectivity data analysis from multiple interfaces:

$$X_{j+1} = \frac{R_{j+1}}{T_{j+1}},$$
(8.14)

$$X_{j} = \frac{X_{j}}{T_{j}} = \exp\left(-2i \ k_{x,j} z_{j}\right) \frac{r_{j,j+1} + X_{j+1} \ \exp\left(-2i \ k_{x,j+1} \ z_{j}\right)}{1 + r_{j,j+1} \ X_{j+1} \ \exp\left(-2i \ k_{x,j+1} \ z_{j}\right)}, \text{and}$$
(8.15)

 $r_{j,j+1}=\frac{k_{z,j}-k_{z,j+1}}{k_{z,j}+k_{z,j+1}}$  being the Fresnel coefficient of the interface j, and  $k_{z,j}=k(n_j^2-\cos^2\!\alpha_i)^{1/2}.$ 

Starting from the fact that there is no reflection from the substrate, i.e.  $R_{N+1} = X_{N+1}$ = 0, the specularly reflected intensity R can be calculated after N iterations.

$$R = |X_1|^2 = |R_1|^2$$
. Since  $R_{N+1} = X_{N+1} = 0$  and  $T_1 = R_1 = 1$ ,  $R_j$  and  $T_j$  inside all layers can be calculated recursively with  $t_{j+1,j} = 1 + r_{j+1,j}$  by,

$$\begin{split} R_{j+1} &= \\ &\frac{1}{t_{j+1,j}} \{ T_j \ r_{j+1,j} \ \exp \left[ \ -i( \ k_{z,j+1} + k_{z,j} \ ) \ z_j \ ], + R_j \ \exp \left[ \ -i( \ k_{z,j+1} - k_{z,j} \ ) \ z_j \ ] \}, \end{split}$$

$$(8.16)$$

$$\begin{split} R_{j+1} = & \\ \frac{1}{t_{j+1,j}} \{ T_j \ r_{j+1,j} \ \exp \left[ -i( \ k_{z,j+1} + k_{z,j} \ ) \ z_j \ \right] + R_j \ \exp \left[ -i( \ k_{z,j+1} - k_{z,j} \ ) \ z_j \ \right] \}. \end{split} \tag{8.17}$$

## 8.1.3 Roughness

To account for the interfacial roughness, instead of the constant refractive index in each layer in the previous section, a continuous variation of the refractive index  $n_j(x, y, z)$  was introduced.

The rough surface is assumed to consist of a collection of smooth interfaces, with

certain z coordinates  $z_j + z$ , weighted by a probability density  $P_j(z)$ . The mean and the root-mean-square roughness are  $\mu_j = \int z P_j(z) dz$  and  $\sigma_j^2 = \int (z - \mu_j)^2 P_j(z) dz$ respectively.

Equations 8.16 and 8.17 are modified to be:

$$\begin{split} R_{j+1} = & \frac{1}{\tilde{t}_{j+1,j}} \{ T_j \; \tilde{r}_{j+1,j} \; \exp \left[ \; -i( \; k_{z,j+1} + k_{z,j} \; ) \; z_j \; \right] + R_j \; \exp \left[ \; -i( \; k_{z,j+1} - k_{z,j} \; ) \; z_j \; \right] \}, \end{split}$$

$$(8.18)$$

$$T_{j+1} = \frac{1}{f_t \ \tilde{t}_{j+1,j}} \{ T_j \exp \left[ i(k_{z,j+1} - k_{z,j}) z_j \right] + R_j \ f_r \ \tilde{r}_{j+1,j} \exp \left[ i(k_{z,j+1} + k_{z,j}) z_j \right] \}.$$
(8.19)

For x-rays,  $f_r$  and  $f_t$  can be set to unity. For a continuous refractive index profile between the layers j and j+1 is assumed with a Gaussian probability density,

$$n_{j}(z) = \frac{n_{j} + n_{j+1}}{2} - \frac{n_{j} - n_{j+1}}{2} \operatorname{erf}(\frac{z - z_{j}}{\sqrt{2}\sigma_{j}}).$$
(8.20)

The resulting modified Fresnel formulas would be,

$$\tilde{\mathbf{r}}_{\mathbf{j},\mathbf{j}+1} = \mathbf{r}_{\mathbf{j},\mathbf{j}+1} \exp\left(-2 \mathbf{k}_{\mathbf{z},\mathbf{j}} \mathbf{k}_{\mathbf{z},\mathbf{j}+1} \sigma_{\mathbf{j}}^{2}/2\right),$$
(8.21)

$$\tilde{t}_{j,j+1} = t_{j,j+1} \exp \left[ + (k_{z,j} - k_{z,j+1})^2 \sigma_j^2 / 2 \right].$$
 (8.22)

# 8.2 Experimental

The model polymer / PAG system described in Chapter 2 was used for all experiments. The substrates were single side polished p-type(100) silicon wafers, cleaned with Piranha solution for 5 minutes. Resist solutions were prepared for conditions similar to all the nanopatterned samples. The resist was spun casted on clean silicon substrates with thickness 70 nm, which was consistent with the thickness of the nanopatterned samples. The samples were then post apply beaked 2 min at 130°C for solvent evaporation. Samples were irradiated using 254 nm UV source with a 19.5 mJ/cm<sup>2</sup> dose which was the minimum dose which ensured 100% dissolution. Each set of data included two control samples: a sample which was not irradiated or post exposure baked, and a sample irradiated but not post exposure baked. The remaining samples were post exposure baked to a given temperature and a time.

#### 8.2.1 X-ray Reflectivity Experiments

X-ray reflectivity (XRR) experiments were conducted at XOR beamlines 8-ID-E at the Advanced Photon Source (APS) of Argonne National Laboratory, with x-ray energy 7.5 keV ( $\lambda = 0.172$  nm). The angle of incidence was varied 0.002° - 0.018° and the reflected intensity at the pin diode was recorded.

## 8.3 Data Analysis

We used nonlinear regression to fit the data to the Parratt recursions in Equation 8.18 and Equation 8.19 in Matlab. The fit parameters were film thickness, air-polymer interfacial roughness, data scale, sample illumination factor and the scattering length density (sld) of the substrate, while the sld of the polymer kept constant. Figure 8.3 illustrates a sample reflectivity spectra and the best fit. The calculated scattering length densities for the protected and deprotected polymer is illustrated in Figure 8.4. We observed a change in sld between the protected and the deprotected polymer samples. However, a trend with post exposure bake conditions was not observed. These values can be used as direct input to the scattering data analysis.



Figure 8.3: X-ray reflectivity spectra from a sample post exposure baked at 90°C for 10 sec.  $\alpha_{c,polymer}$  and  $\alpha_{c,si}$  denote the critical angle of the polymer and the silicon substrate respectively.



Figure 8.4: Calculated scattering length densities for all the post exposure bake conditions.

# Chapter 9 Small angle X-ray Scattering

Small angle x-ray scattering (SAXS) can be used to characterize ordered structures where there are density inhomogeneities exist. Therefore this is a very good technique to measure the depth dependant resolution of the CA resist nanostructures as well as the ordered block copolymer domains. In this chapter we discuss the principles of SAXS, the form factor and the interface function calculation and the adopted data analysis techniques.

## 9.1 Concept

When electron density inhomogeneities of colloidal size exist in the sample, small angle x-ray scattering can always be observed. Incoherent scattering is negligibly weak at very small angles. When x-rays pass through objects, electrons resonate with the x-ray frequency and emit small coherent secondary waves, and interfere with each other. Photon energy of x-rays are much larger than the binding energy of light atoms, all electrons will behave as they are free. The scattered waves are coherent, therefore the scattered amplitudes (A) can be added, and the intensity is given by  $|A|^2$ . The scattered amplitudes are equal in magnitude, and differ in their phase ( $\psi$ ) which depends on the position of the electron in space [101].

Figure 9.1 illustrates the interference between the waves originating at two particles O and P where O is taken as the reference particle. The direction of the incident beam is denoted by the unit vector  $\mathbf{k}_i$  and the scattered beam by  $\mathbf{k}_f$ . The path difference of the point P (**r**) is  $-\mathbf{r}(\mathbf{k}_f - \mathbf{k}_i)$ . Therefore,  $\psi$  can be calculated as  $-(2\pi/\lambda) \mathbf{r}(\mathbf{k}_f - \mathbf{k}_i)$ , which takes the form  $\varphi = -(2\pi/\lambda)\mathbf{qr}$ . It can be observed from the Figure 9.1 that  $\mathbf{k}_f - \mathbf{k}_i$  lies symmetrically with respect to the incident and scattered beam, with a magnitude of  $2 \sin\theta$ , where  $2\theta$  is the scattering angle.

All scattering measurements on an object can be limited to the determination



Figure 9.1: Interference between the waves originating at two scattering centers.

of the scattered intensity, I for all possible values of  $\mathbf{q} = 2\sin\theta/\lambda$ . Scattered intensity  $I(\mathbf{q})$  is represented in the reciprocal space, where for each point of the space there corresponds a vector  $\mathbf{q}$  which is equal to the vector between the origin and that point. To understand the dependance of the diffracted intensity on the direction of the vector  $\mathbf{q}$ , Figure 9.2, from point  $\mathbf{K}_i$  which is chosen as the origin of the reciprocal space, define a vector  $\mathbf{K}_i \mathbf{O} = -\mathbf{K}_i/\lambda$ . If we draw a sphere using O as the origin and radius  $1/\lambda$ , for any given direction of observation,  $\mathbf{OK}_{\mathbf{f}} = \mathbf{q}/\lambda$  is located on the sphere, which is called the "Edwald sphere," and  $\mathbf{K}_i \mathbf{K}_{\mathbf{f}}$  represents the vector  $\mathbf{q} = (-\mathbf{K}_i - \mathbf{K}_f)/\lambda$  [102, 103].

#### 9.1.1 Scattered Intensity

Summation of the resulting amplitudes can be represented by,  $\exp(-i\mathbf{qr})$ . If we define electron density as the number of electrons per unit volume, then a volume element dV at a position r contain  $\rho(\mathbf{r})dV$  electrons. Therefore, the amplitude of diffraction (F) in a given direction (**q**) can be given by [101],

$$F(\mathbf{q}) = \int \int \int d\mathbf{V} \cdot \rho(\mathbf{r}) \, e^{(-i\mathbf{q}\mathbf{r})}, \qquad (9.1)$$



Figure 9.2: Reciprocal space explored by sections through the Edwald sphere (Guinier 1955).

and this is the 3-dimensional Fourier transform of the electron distribution within the object. The resulting intensity again is a Fourier integral involving the relative distance  $(r_1 - r_2)$  [101],

$$I(\mathbf{q}) = FF^* = \int \int \int \int \int \int dV_1 \cdot dV_2 \cdot \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) e^{(-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2))}, \qquad (9.2)$$

If every electron pair with relative distance  $\mathbf{r}$  can be represented by a point in space, the density is given by:

$$\overline{\rho}^2(\mathbf{r}) = \int \int \int d\mathbf{V}_1 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2), \qquad (9.3)$$

with  $r = (r_1 - r_2)$  constant.

The intensity distribution in the reciprocal space,  $\mathbf{q}$ , is uniquely determined by the electron structure of the object  $\overline{\rho}^2(r)$  as,

$$\mathbf{I}(\mathbf{q}) = \mathrm{dV} \cdot \overline{\rho}^2(\mathbf{r}) \cdot \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{r}}.$$
(9.4)

Therefore, the structure of an object can be obtained from the inverse Fourier transform of its intensity distribution,

$$\overline{\rho}^2(\mathbf{r}) = (1/2\pi)^3 \int \int \int d\mathbf{q}_{\mathbf{x}} d\mathbf{q}_{\mathbf{y}} d\mathbf{q}_{\mathbf{z}} \cdot \mathbf{I}(\mathbf{q}) \cdot e^{-i\mathbf{q}\mathbf{r}}.$$
(9.5)

For a statistically isotropic system, the electron density distribution  $(\rho^2(\mathbf{r}))$  depends only on the magnitude of  $\mathbf{r}$  of the distance. Therefore,  $e^{-iqr}$  can be replaced by the average taken over all directions of  $\mathbf{r}$  [101].

$$\langle e^{-i\mathbf{q}\mathbf{r}} \rangle = \frac{\sin (q\mathbf{r})}{q\mathbf{r}},$$
(9.6)

and

$$I(\mathbf{q}) = \int 4\pi r^2 d\mathbf{r} \cdot \overline{\rho}^2(\mathbf{r}) \frac{\operatorname{sinqr}}{\operatorname{qr}}.$$
(9.7)

It is assumed in small angle scattering that no long range order exists, i.e. no correlation between two points separated widely enough. Thus at larger distances the electron densities should become independent and can be replaced by the mean density  $\overline{\rho}$ . Thus the autocorrelation function in Equation 9.3 need to tend towards a constant  $\nabla \overline{\rho}^2$  with the maximum being at r = 0. The structure is therefore defined at a finite region only, where  $\nabla \overline{\rho}^2$  deviates from the final value [101].

Therefore, the electron density fluctuation,  $\eta = \rho - \bar{\rho}$  being used instead of

density itself and the autocorrelation in Equation 9.3 is rephrased as [104],

$$\bar{\eta}^{*2} = \bar{\rho}^2 - V\bar{\rho}^2 = V \cdot \gamma(r), \qquad (9.8)$$

where

$$\gamma(r) = \langle \gamma(r_1)\gamma(r_2) \rangle,$$

which gives the scattered intensity in the form,

$$I(\mathbf{q}) = \int_{v} (\Delta \eta^{*2}) \exp (2\pi i \mathbf{qr}) \, dv_{r}.$$
(9.9)

# 9.2 Width of density transition

Equation 9.9 above assumes that there is an infinitely sharp density transition from one phase to another in a two phase system. However, in practice at minimum, the density transition has the width produced by the electron distribution of the basic structural elements of the two phases. [104–106] This can be visualized as the convolution of the ideal density distribution ( $\eta$ ) with a 'smoothing function' (h) so that,

$$\eta_{obs} = \eta * h. \tag{9.10}$$

Therefore where H is the Fourier transform of h, the observed scattered intensity becomes,

$$\mathbf{I}_{\rm obs} = \mathbf{I} \cdot \mathbf{H}^2. \tag{9.11}$$

Overall, therefore, the scattered intensity can be expressed as:

Intensity = Line Grating  $\times$  Shape Function  $\times$  Roughness Function,

$$\mathbf{I}(\mathbf{q}) = \sum_{n=-\infty}^{n=\infty} \delta(\mathbf{q}_{y} - \frac{2\pi n}{d}) \cdot |\mathbf{P}(\mathbf{q})|^{2} \cdot |\mathbf{H}(\mathbf{q}, \Delta)|^{2}, \qquad (9.12)$$

$$P(\mathbf{q}) = \int s(\mathbf{r}) e^{-\mathbf{q}\cdot\mathbf{r}} dv, \qquad (9.13)$$

$$H(\mathbf{q}, \Delta) = \exp\left(\frac{-\Delta^2 \mathbf{q}_y^2}{4}\right). \tag{9.14}$$

**CA Resist Interface** The deprotected-protected polymer transition was modeled as an error function centered at y = 0 with a probability density function P(y) with an interfacial half width of  $\sigma$ :

$$\operatorname{erf}(y) = \frac{2}{\pi} \int_0^y e^{-x^2} dx,$$
 (9.15)

$$P(y) = \frac{1}{\sigma\sqrt{2\pi}} \exp[\frac{-y^2}{2\sigma^2}].$$
 (9.16)

With the probability distribution of

$$\frac{1}{2} erf[\frac{y}{\sqrt{2}\sigma}]. \tag{9.17}$$

Fourier transform of the above results in the interface function,

$$H(q,\Delta) = \frac{\exp[-\frac{1}{2}q_y^2 \sigma^2] |\sigma|}{\sqrt{2\pi} \sigma}.$$
(9.18)

**Block Copolymer Interface** The poly(styrene-methylmethacrylate) (PS/PMMA) block copolymer interface has been successfully modeled as a diffuse composition profile with a finite width  $\Delta$  [107].

The composition of the PS phase across the interface plane positioned at x = 0is  $\rho_{PS}(x) = 0.5[1 + tahn(2x/\Delta)]/\Delta$  [105]. The resulting smoothing function and the interface function would be:

$$h_1(x) = [\operatorname{sech}^2(2x/\Delta)]/\Delta, \qquad (9.19)$$

$$H(q,\Delta) = \frac{\pi\Delta q_y}{4} \operatorname{csch}(\frac{\pi\Delta q_x}{4}).$$
(9.20)

#### 9.2.1 Shape Function

As explained in Equation 9.1, the amplitude of diffraction in a given direction is the 3-dimensional Fourier transform of the electron distribution within the shape of the object. The structure of an object can be explained as a homogeneous finite volume cut out from an infinite homogeneous matter. Therefore the density inside the object can be expressed as [102],

$$\rho(x) = \rho_{\infty}(x)\sigma(x), \qquad (9.21)$$

where  $\rho_{\infty}(x)$  is the electron distribution function in the infinite matter and  $\sigma(x)$  being the form factor of the object which is unity inside the external surface of the object and zero outside.

Therefore, calculation of the shape function involves, determining the shape of the object and taking its Fourier transform. Determination of the shape of the cross section depends on the system being studied. The cross sections of our resist nanolines and block copolymer domains can simply be best described by one or more trapezoids. A set of trapezoids stacked on top of each other can be used to describe the changes in the sidewall angle through the depth of our thin films. Form factor (shape factor) calculation of a single trapezoid (Figure 9.3) is described below:



Figure 9.3: Trapezoidal cross section.

And thus the form factor for a trapezoidal cross section can be calculated as [108]:

$$\mathbf{x}' = \mathbf{z} \, \tan \phi, \tag{9.22}$$

$$w(z) = w_z - z \tan\phi. \tag{9.23}$$

Since the length of our line gratings were  $20\mu m$ , 2-dimensional shape can be assumed based on the dimensions: i.e., the lines are infinitely long compared to the height and the width. The simplified form factor for a trapezoidal shape is described below: Substituting in Equation 9.1,

$$\mathbf{F}(\overline{\mathbf{q}}) = \Delta \rho(\mathbf{z}) \int_0^H \int_{-w}^w \int_{-L}^L e^{(-\mathbf{i}(\mathbf{q}_{\mathbf{x}}\mathbf{x} + \mathbf{q}_{\mathbf{y}}\mathbf{y} + \mathbf{q}_{\mathbf{z}}\mathbf{z}))d\mathbf{x} d\mathbf{y} d\mathbf{z})}, \qquad (9.24)$$

$$= \Delta \rho(\mathbf{z}) \frac{2\mathrm{sin}(\mathrm{Lq}_{\mathbf{x}})}{q_{\mathbf{x}}} \int_{0}^{H} \int_{-w}^{w} \mathrm{e}^{(-\mathrm{i}(q_{\mathbf{y}}\mathbf{y}+q_{\mathbf{z}}\mathbf{z}))\mathrm{d}\mathbf{y} \, \mathrm{d}\mathbf{z}}, \qquad (9.25)$$

$$= \Delta \rho(\mathbf{z}) \frac{2\mathrm{sin}(\mathrm{Lq}_{\mathbf{x}})}{q_{\mathbf{x}}} \int_{0}^{H} \frac{2\mathrm{sin}(\mathrm{wq}_{\mathbf{y}})}{q_{\mathbf{y}}} e^{(-\mathrm{i}(q_{\mathbf{z}}\mathbf{z}))\mathrm{d}\mathbf{z}}, \qquad (9.26)$$

where  $w = w_z - z \tan \phi$ .

## 9.2.2 Determination of Pattern Cross Section

The determination of the cross section of the grating lines require the measurement of the scattered intensity in the  $q_y - q_z$  plane. There are several approaches to probe the  $q_z$  dependance of the scattering intensity: measure the scattering at a very large scattering angle where the  $q_z$  dependace cannot be neglected, vary the x-ray wavelength resulting in pushing the Edwald sphere forward and backward probing different  $q'_z$ s, and measure the small angle scattering at different sample rotation angles.

Diffraction peaks occur in  $q_y - q_z$  plane at the intersections of the reciprocal lattice and the Edwald sphere. By rotating the sample around its x-axis, the reciprocal space map is rotated with respect to the Edwald sphere (Figure 9.4).



Figure 9.4: Small angle scattering geometry

A line grating aligned along the x-axis produces a one dimensional series of diffraction peaks. For a given rotation angle  $\phi$ , the diffraction peak spacing  $\Delta q$  is inversely proportional to the grating pitch d projected on the detector plane, resulting in  $\Delta q = 2\pi/(d \cos \varphi)$  [109].

The scattered intensity along any axis on the detector represents the Fourier transform of the projection of the lithographic line profile onto the axis. The projection of the line profile onto the detector axis changes with rotation around x-axis. As an example, Figure 9.5 illustrates the projected profiles of a rectangular and a trapezoidal cross section. When the samples are rotated, the projected line profiles onto the detector axis from a rectangle is symmetric thus can be described by a set of even functions, resulting in a summation of cosine functions as its Fourier transform. The projection of the trapezoid is a shape that lacks symmetry thus cannot be solely described by a set of even functions, thus resulting in a dditional sine functions in the Fourier transform. The sine terms contribute to scattering intensities near



Figure 9.5: Projections of a rectangular and a trapezoidal cross sections of rotated nanolines.

even order diffraction peaks resulting in intensity enhancement of the even diffraction orders with rotation. Therefore, it can be noted that the steepness of the sidewall angle contributes to the intensity enhancement at the even diffraction orders [110]. In addition as the sample is rotated, the effective transmission path length (beam footprint) of the x-ray beam through the sample changes as  $t/\cos\phi$ , where t is the substrate thickness which needs to be accounted for [111].

#### 9.2.3 Reciprocal Space

The grating pitch d in real space is inversely proportional to the diffraction peak spacing in reciprocal space. Figure 9.6 illustrates a line grating oriented at a fixed angle  $\alpha$  to the y-axis. Therefore the diffracted image on the detector had a rotation around the z-axis as illustrated in Figure 9.7(left).

For processing purposes, the image is rotated clockwise about [0, 0, 1] axis by



Figure 9.6: Sample rotated at a fixed angle  $\alpha$  to the y-axis.



Figure 9.7: Original diffracted image (left) and the rotated image (right).

an angle  $\gamma$ . (Figure 9.7) It was observed that  $\gamma$  varies from frame to frame, but in each frame, the measured distance *m* from the origin to the first diffraction order remain the same after rotation (Figure 9.8).

Thus, if the incident wave vector in detector coordinates is,

$$k_i = k_o [0, 0, 1].$$
 (9.27)



Figure 9.8: In-plane and the out-of-plane angles at the detector, with respect to the sample.

The resulting diffracted wave vector can be calculated as,

$$k_{f} = k_{o} [k_{x}, k_{y}, k_{z}],$$
 (9.28)

$$\mathbf{k}_{\mathbf{x}} = \sin\alpha, \tag{9.29}$$

$$\mathbf{k}_{\mathbf{y}} = \cos\alpha \sin 2\theta_{\mathbf{m}}, \tag{9.30}$$

$$\mathbf{k}_{\mathbf{z}} = \cos\alpha \, \cos \, 2\theta_{\mathbf{m}}, \tag{9.31}$$

where,

$$q_{detector} = (k_f - k_i). \tag{9.32}$$

Therefore the reciprocal space vectors are,

$$q_{x,detector} = (2\pi/\lambda) \sin\alpha,$$
 (9.33)

$$q_{y,detector} = (2\pi/\lambda) \cos\alpha \cos 2\theta$$
, and (9.34)

$$q_{z,detector} = (2\pi/\lambda) \left[ -1 + \cos\alpha \, \cos 2\theta \right]. \tag{9.35}$$

The  $\varphi$  rotation in the sample space projects to the detector space as a rotation along the x-axis. (Figure 9.5). Applying the rotation matrix by angle  $\varphi$  counterclockwise along [1, 0, 0] to represent depth dependence the reciprocal space vectors are being calculated:

$$q_{x} = (2\pi/\lambda)\sin(\alpha), \qquad (9.36)$$

$$q_{y} = (2\pi/\lambda)[\cos(\alpha)\sin(2\theta - \varphi) + \sin(\varphi)], \qquad (9.37)$$

$$q_z = (\pi/\lambda) [\cos(\alpha + 2\theta - \varphi) - 2\cos(\varphi) + \cos(\alpha - 2\theta + \varphi)].$$
(9.38)

# 9.3 Modeling

An inverse calculation method was followed to analyze the scattering data. First, the domain shape is approximated. Based on the above, the scattering profile is simulated, and further refined using nonlinear regression. The resulting domain shape is then used as an input to a "Simulated Annealing" program which further refined and evaluated the results.

#### 9.3.1 Nonlinear Regression

Nonlinear regression (NLR) is a paramount tool for fitting data to any selected equation to determine one or more parameters. NLR procedures determine the values of the parameters that minimizes the sum of the squares (SS) of the distances of the data points to the curve:

$$SS = \sum (y_{data} - y_{curve})^2.$$

NLR problems are iterative, and requires an initial best estimate (initial guess) of the value of each parameter. NLR refines these values to improve the fit of the curve to the data. The iteration procedure continues until negligible improvement occurs. There are several techniques to calculate the iterations. We use "nlinfit" in Matlab, which accommodates the standard Levenberg-Marquardt method, which combines the steepest descent and Gauss-Newton methods. The method of steepest descent works best in initial iterations while the Gauss-Newton method in later iterations. Levenberg-Marquardt method emphasizes the steepest descent method in initial steps till the residual sum of the squares decreased considerable and gradually switches to the Gauss-Newton method when the sum of the squares of the steepest descent method is no longer decreasing [112].

Nonlinear regression results need to be carefully interpreted due to several concerns: Overflow/ underflow of data, ill-conditioned system or a singular matrix can cause termination of the calculations without convergence, too many fit parameters can slow down or fail to converge. Additionally, when trying to fit multiple variables it can converge to a local minima failing to produce the best fit. Nonlinear regression result in multiple solutions and was found to be very time consuming. Therefore, nonlinear regression was only used in simulating the domain shape.

#### 9.3.2 Simulated Annealing

Simulated annealing is an optimization technique that has attracted significant attention for large-scale optimization problems. It is an analogy with thermodynamics, to the cooling and crystallization of metals and some liquids. At higher temperatures the molecules are free to move, but as the temperature is decreased the mobility is lost lining up in a rigid structure. The minimum energy state can be achieved upon slow cooling, allowing ample time for the redistribution of molecules [113].

## Algorithm

Consider a succession of decreasing temperatures, starting from a temperature  $T_o$ . At each temperature T, the system is allowed to reach its thermal equilibrium. The probability of the system is in some state with energy E can be expressed using Boltzmann distribution with a normalization function of Z(T) and Boltzmann constant  $k_b$ ,

$$P(E = k) = \frac{1}{ZT} \exp(-\frac{k}{k_b T}).$$
 (9.39)

As T decreases, the range of the Boltzmann distribution concentrates on the states with the lowest energy, eventually "freezing" the system as T becomes very low. If the temperature is reduced sufficiently slowly (annealed) this frozen state will have its minimum energy. Boltzmann constant relates temperature to energy, i.e., the system can sometimes go uphill, but the lower the temperature, it becomes less likely.

Metropolis et. al [114], incorporated the above into numerical calculations: given a current state of the system with energy  $E_0$ , choose a new state by displacing a randomly chosen particle. If  $E < E_0$ , where E is the energy of the new state, then the system remains at the new state, and another state is selected as above. Yet if  $E \ge E_0$ , the probability of remaining in this new state would be  $\exp[-(E - E_0)/kT]$ . Kirkpatric et al. (1983) introduced an annealing schedule which defines how the temperature is decreased. Beginning with a high temperature  $T_o$ , the Metropolis algorithm is followed until equilibrium is reached. According to the annealing schedule the temperature is then decreased, and Metropolis algorithm is followed at the new temperature until equilibrium is reached. The procedure is repeated until the system freezes.

# Chapter 10 Depth Dependent Resolution in Chemically-Amplified Resists

The focus of our work is to determine the three-dimensional resolution of lithographically formed nanopatterns in a thin polymeric film. Sample preparation for SAXS measurements was detailed in Chapter 6. In Chapter 8 we calculated the scattering length density which is proportional to the electron density at each post exposure bake condition. Chapter 9 discussed the use of SAXS to determine the depth dependant resolution of a nanopatterned polymer film and the data analysis techniques. This chapter details the data processing methodology from SAXS data acquisition and modeling followed by a discussion on our approach to use Monte Carlo simulations to interpret the experimental data.

# 10.1 Experimental

#### **10.1.1** Sample Preparation

The aim of this work was to measure the dependance of the depth dependant resolution to the PEB conditions. PAG concentration in the resist formula was 4 wt% of the weight of the polymer resin. Nanopatterned samples were PEB at temperatures 90°, 100°, 110°, 120° and 130° and PEB times 10, 15 and 20 sec using the process detailed in Chapter 6.

#### 10.1.2 SAXS Data Acquisition

The structure of CA resist line gratings was characterized with variable-incidentangle SAXS [109, 111]. Experimental process limits the lowest achievable grating pitch to be 170 nm. Diffraction peak spacing is inversely proportional to the grating,  $\Delta q = 2\pi/d \cos\varphi$ , where  $\phi$  is the angle of rotation [109]. The width of the beam stop was larger than the distance between two diffraction orders such that it was blocking the first and the second diffraction orders from being visible. However, if the sample was rotated at a fixed angle  $\alpha$  around its x-axis (Figure 9.6 Chapter 9), the second diffraction order could be visible. Diffracted intensity was measured as a scan, each having 30 image frames as a function of rotation angle ( $\varphi$ ) -5<sup>o</sup> - 45<sup>o</sup> in increments of 1.6667<sup>o</sup>. Each measurement samples an area of 50  $\mu$ m x 100  $\mu$ m, the dimensions of the beam. Each diffracted frame is recorded as a 2048 x 2048 16-bit TIFF image in a 2-dimensional detector.

# 10.2 Image Analysis

A sample diffracted image for an angle of rotation  $\varphi = 5^{\circ}$  for a sample PEB 20 sec at 110°C is illustrated in Figure 10.1(a). Each frame was rotated along the [0, 0, 1] axis by an angle  $\gamma^{\circ}$  till all the Bragg peaks position on the same horizontal axis (Figure 10.1(b)), and as explained in Chapter 9, the distance from the origin to the diffraction order still remain the same. The intensity of each peak was extracted and summed over a 5-pixel width vertically to obtain a line profile using the image processing software IDL (Figure 10.2(a)).



Figure 10.1: A single diffracted image associated to  $\varphi = 5^{\circ}$ : (a) Original image recorded in the detector, (b) Image after rotating  $\gamma^{\circ}$ so that the diffraction peaks fall on a horizontal line.



Figure 10.2: (a) Line profile extracted from the Figure 10.1(b) above, (b) Contour image of the extracted line profiles from all frames for a sample.

The resulting output, which is a 2-dimensional contour image of  $\varphi$  rotation, peak position and intensity is presented in Figure 10.2(b). The above was used in a Matlab script which extracted each line profile and individually corrected the background based on a set of user specified baseline points. Baseline corrected data was used in another Matlab script which generated a contour map of  $q_{ll}(\sqrt{q_x^2 + q_y^2})$ ,  $q_z$  and intensity (Figure 10.3).

A "point-and-click" routine in Matlab was written to extract the intensity and the position of each Bragg peak. Peak intensity was extracted as a horizontal summation of 5 pixels around the center of each peak position. Figure 10.4 illustrates a sample of the extracted data plotted as a function of intensity for each diffraction order.



Figure 10.3: Contour map of reciprocal space vectors  $(q_{ll},qz)$  and intensity. Note that n = 1 - 5 denotes the diffraction order. The first order was not clearly visible in most frames being blocked by the beamstop.



Figure 10.4: Extracted shape profiles of the diffraction peaks.

**Control Samples** Since polymeric materials can be irradiated by ionizing radiation such as x-rays, a set of control measurements were taken to verify the absence of such radiation damage in our nanostructures : (a) Multiple scans were taken on the same location of the nanograting at the same scan direction, Figure 10.5, and (b) a second scan on the sample at a different nanograting location was taken and compared with each other. In addition, in some of the samples the direction of scan was reversed, i.e., 45 to  $-5^{\circ}$  to verify the consistency of the nanopatterns (Figure 10.6).



Figure 10.5: Peak shape profiles of two scans measured on the same direction of rotation at the same location of the nanograting.



Figure 10.6: Peak shape profiles of two scans measured reverse directions of rotation at a different location of the nanograting.

Film Thickness The overall height of the deprotection regions were measured by spin casting a resist film using the same recipe and patterning an array of 10  $\mu m$  x 10  $\mu m$  squares within the membrane. After post exposure bake at 130°C for 20 sec and developing in 0.062N TMAH, the patterns were imaged using atomic force microscopy (Figure 10.7). The calculated average film thickness was 55 nm.

**Topography** High-resolution AFM images were used to determine the shapes of the surface "bumps" from deprotection. Surface topography was best described as 4 trapezoids stacked on top of each other. The height of each trapezoid was chosen based on the shape of each profile.



Figure 10.7: AFM micrograph of a developed 10  $\mu m$  wide square pattern.



Figure 10.8: High resolution AFM micrograph of a latent image (top). Extracted line profile of the surface topography and the 4-trapezoid fit (bottom).

# 10.3 Data Modeling

Seven diffraction orders were clearly observable in our data, out of which five peaks displayed clearly defined intensity profiles. The first diffraction order was distorted at lower  $\varphi$  angles due to its relative position with the beam stop, therefore ignored from data analysis purposes. As described above, due to its limitations nonlinear regression was only used for simulation purposes, and simulated annealing was adopted for further refining the parameters. For the ease of modeling, nonlinear regression and the simulated annealing scripts were programmed to describe the protected domains.



Figure 10.9: Line shape function (left) and the interfacial function (right).

The lineshape function was designed as a set of four trapezoids stacked one on top of each other, Figure 10.9. The surface topography was modeled as described above using four trapezoids. The deprotection interfacial function being used in the calculations is explained in Chapter 9. Diffracted intensity is a function of the line grating, shape function and the interfacial function. The Fourier transform of the shape function was convolved with the interfacial function to simulate the diffracted intensity and further refinement. The best fit to a line shape model for a sample PEB at 110°C for 20 sec is reported in Figre 10.10, with the calculated profile.



Figure 10.10: Diffraction peak profiles and the refined simulated annealing results of a sample PEB at  $110^{\circ}$ C for 20 sec. The calculated deprotection depth profile is shown at the lower right.

# 10.4 Results

Results from SAXS data modeling in Figure 10.11 illustrates the calculated line shape profiles as a function of PEB temperature. These demonstrate that the image resolution can vary through the thickness of the film. The domain shape varies with distance from the free surface and substrate interfaces, producing a sidewall angle of approximately  $30^{\circ}$ . This is a consequence of a broader reaction front at the free surface compared with the substrate-polymer interface. Such depth-dependant image resolution is detected for all bake temperatures and times that was studied. There was no observed clear trend of the width of the deprotected profiles with bake temperature. We believe that the slow mobility of the polymer at lower bake temperatures slow down the catalyst diffusion. At temperatures close to the polymer's  $T_g$ , the increased polymer mobility result in increased diffusion thus higher levels of deprotection. Having very long catalyst chain lengths, CA resist are very sensitive. Therefore we did not detect a trend with post exposure bake time at our range of interest, which were much larger time scales relative to the acid sensitivity.



Figure 10.11: Depth dependant resolution of nanogratings as a function of PEB temperature.

In addition the deprotected polymer interfacial width was also calculated from the scattering data analysis (Figure 10.12). We observed an increase in interfacial width with bake temperature. Such behavior can be attributed to the increasing free volume expansion within the film with bake temperature. Currently, analysis of experimental data assumes a constant interfacial width through the depth of the film.



Figure 10.12: Width of the deprotected interface as a function of bake time.

# 10.5 Simulations

Monte Carlo simulations were performed in collaboration with Doxastakis group at University of Houston. Lattice kMC simulations were designed to quantitatively model experimental data. The key aspects of the kMC model for deprotection are illustrated in Figure 10.13: Simulations are based on a three-dimensional lattice of 140 cells  $\times$  50 cells  $\times$  80 cells, where each cell represents a volume of 1 nm  $\times$  1 nm  $\times$  1 nm. A cell with an acid molecule can undergo a deprotection reaction with rate  $k_p$ . An additional reaction with rate  $k_T$  describes the transformation of a deprotected cell to a trapping cell. Acid molecules translate with jump frequencies that relate to macroscopic diffusion coefficients  $D_1$  and  $D_2$  for protected and trapping cells, respectively, where  $D_2$  is currently set to zero. Simulations were implemented as described by Chatterjee and Vlachos using OpenMP for multicore CPU architectures [115].
We hypothesized that depth-dependent image resolution is associated with depth-dependent acid diffusion rates (due to confined polymer dynamics), a surface excess of acid catalyst, or a combination of these factors. To simulate depth-dependent diffusion rates, the initial acid distribution was located at x = 0 with a width of 40 nm, and the simulation cells were divided into three regions where diffusivity decreased with increasing distance from the free surface. To simulate a surface excess of catalyst, three acid densities were assigned that decreased with distance from the free surface, while acid diffusivity was constant throughout the film thickness.

In summary, experimental results demonstrate that image resolution can vary with distance from the free surface and substrate interfaces, producing a sidewall angle of approximately 35°C. Simulations could explain the origins of this phenomena. Figure 10.13(b) compares the deprotection profiles due to depth-dependent diffusion rates and a surface excess of acid catalyst. These simulations demonstrate that both behavior can produce depth-dependent image resolution. However, we note that enhanced acid diffusivity at the free surface will also generate a broader deprotection interface.



Figure 10.13: (a) Processes that are employed in the simulation. (b) 2-D density maps showing spatial variation in deprotection fraction at 15 seconds. a) Incorporating an excess of acid at the film surface; b) Incorporating variable diffusion rate through the film thickness. Both features can produce depth-dependent image resolution.

# Chapter 11 Measuring the Three Dimensional Structure of Block Copolymer Line Gratings

The performance of semiconductor devices is determined by the density of patterned features, whether it be individual transistors in a microprocessor or discrete bits in a high-capacity hard disk drive. As the sizes of patterned features approach 10 nm, the nanopatterning industry is looking to augment traditional optical lithography with new materials and processes. There are a handful of candidate "alternative" technologies competing at the 10 nm node, including direct-write electron beam lithography, nanoimprint lithography, and directed self-assembly (DSA) of block copolymers. Each of these alternative lithographic techniques will likely enter the manufacturing process as a complement to established lithographic tools.

For example, DSA can improve the quality of optically-patterned resists by shrinking pattern dimensions, increasing pattern density, and potentially "healing" defects [7,116–118]. However, there is evidence from simulations [119] and experiments [107, 120] that polymer-substrate interactions can deform the domain shapes. This behavior can be challenging for manufacturing because domain widths must be uniform through the film thickness for reliable pattern transfer by plasma etching. In this chapter, we use transmission small-angle X-ray scattering (SAXS) to measure the three-dimensional shape of poly(styrene-*b*-methyl methacrylate) (PS-PMMA) line gratings. Experimental data are interpreted with the aid of numerical simulations based on self-consistent field theory (SCFT). The concerted experimental and modeling effort demonstrates that DSA pattern quality is strongly affected by the types of interactions at each interface.

# 11.1 Experimental Section



Figure 11.1: (a) Tapping-mode atomic force microscopy measurement of the block copolymer grating (height image). Dark and bright domains are PS and PMMA, respectively, (Vu, et.al,2011) where PMMA domains are ca. 2 nm taller than PS. Inset: Schematic of the sample cross-section. (b) Illustration of SAXS geometry. The scattering vector is  $\vec{q} = \vec{k_f} - \vec{k_i}$ .

Fabrication of epitaxial templates, characterization of epitaxial templates, and DSA of the PS-PMMA lamellae is discussed elsewhere. [107] These procedures are very similar to work from Nealey et al. [119]. Note that PS-attractive stripes are PS brush, and PMMA-attractive stripes are oxidized PS brush. These chemical patterns have minimal topography (less than 1 nm height variation).

Variable-incident-angle SAXS measurements were implemented at the Advanced Photon Source of Argonne National Laboratory (beam line 8-ID-E). Samples were placed in a vacuum chamber and illuminated with 7.35 keV radiation at incident angles ( $\Phi$ ) in the range of -45° to 45° with increments of 1.3°. The scattering was recorded with a Pilatus 1MF pixel array detector (pixel size = 172  $\mu$ m) positioned 2175 mm from the sample. Acquisition times were 10 sec per angle. The beam spot size was 150  $\mu$ m wide by 50  $\mu$ m tall. Data were corrected for changes in illuminated volume as a function of  $\Phi$ .

For SAXS data analysis, we calculated the area under each primary peak as function of incident angle  $\Phi$  and scattering angle  $2\Theta$ . These data are then mapped to  $(q_x, q_z)$  coordinates following the definitions in Figure 11.1(b). All data are background corrected to remove the parasitic scattering at low  $q_x$  values.

The samples considered in this report are thin films of lamellar PS-PMMA copolymers cast on chemo-epitaxial templates. The PS-PMMA copolymer was purchased from Polymer Source with a molecular weight of  $M_n$ =100 kg/mol, polydispersity index of 1.12, and composition of 50% PS by volume. The equilibrium lamellar periodicity is  $L_0 = (46 \pm 1)$  nm at 240°C. All copolymer films were  $(64 \pm 1)$  nm thick and annealed at 240°C for 6.5 minutes. The epitaxial templates were fabricated with electron-beam lithography and consist of alternating hydrophobic and hydrophilic lines with a 46 nm pitch. The hydrophobic and hydrophilic patterns are selective towards PS and PMMA, respectively, and the width of the PS-selective stripe ranges from  $w_{PS} \approx 0.55L_0 - 0.63L_0$  [107]. Figure 11.1a includes a schematic of the PS-PMMA line grating and a representative micrograph of the film surface.

# 11.2 CDSAXS Measurements

The structure of PS-PMMA line gratings was characterized with variableincident-angle SAXS, also known as "critical-dimension" SAXS [109,111]. The measurement geometry is illustrated in Figure 11.1b. The sample is illuminated at an angle of incidence  $\Phi$ , which is varied through a range of  $\pm 45^{\circ}$  for depth sensivity [111], and the scattered intensity is recorded as a function of diffraction angle 2 $\Theta$ . Detailed illustration of the scattering theory, model and the fit procedure is presented in Chapter 9.

All data are mapped from  $I(2\Theta, \Phi)$  to  $I(q_x, q_z)$  coordinates for comparison with scattering models. 11.2a includes an example of the data extracted from a single SAXS measurement, and Figure 11.2(b-f) reports the scattering profiles  $I(q_z)$  for five orders of diffraction peaks  $q_x = 2\pi n/L_0$ . The three-dimensional shape of the PS-PMMA lamellae was calculated from SAXS data through an inverse solution method. First, the lamellar structure was described by a model that includes the size, shape, and periodicity of the domains, as well as the apparent width of the copolymer interface [107]. The line shape s(x, z) is approximated by a stack of four trapezoids as illustrated in Figure 11.3(a). Second, model parameters were refined to obtain agreement between predicted and measured SAXS profiles. This refinement was implemented with a simulated annealing (Monte Carlo) algorithm [72]. The solid line in Figure 11.2(b-f) is the average predicted scattering profile from a minimum of 25 runs, and the error bars encompass  $\pm 1$  standard deviation.



Figure 11.2: (a) Line profile  $I(q_x)$  from data acquired at  $\Phi = 0$   $(q_z \approx 0)$ . Five orders of diffraction peaks are observed, along with weak satellites that are associated with noise in the epitaxial template (Perera, et.al,2010). (b-f)  $I(q_z)$  for five diffraction orders, i.e.,  $q_x = 2\pi n/L_0$ . Open symbols are experimental data, and solid line is the best-fit line shape model.



Figure 11.3: (a) Line shape model s(x, z) for analysis of SAXS data. The total height is constrained, but the height, width, and slope for each trapezoid can vary as illustrated by the arrows. (b) Block copolymer domain shape calculated from SAXS analysis. (c,d) Simulated domain shape for a pattern duty cycle of  $w_{PS}/L_0 = 0.7$ .

Figure 11.3(b) reports the block copolymer domain shapes that were extracted through analysis of SAXS data. Each curve represents the average line shape with error bars that encompass  $\pm 1$  standard deviation. When calculating the shape function from SAXS data, there are two planes of symmetry that lead to degenerate solutions - so one cannot distinguish between up/down (180° rotation about the *x*-plane) or left/right (180° rotation about the *z*-plane). Therefore, all profiles in Figure 11.3(b) were transposed so they overlap. The dimensions of the epitaxial template are different for each sample, where  $w_{PS}/L_0$  is estimated to range from 0.55 up to 0.63 [107], but the resulting domain shapes are very similar. All samples exhibit a large "foot" near one interface and a more subtle "rounding" near the other. One could infer that the large "foot" is associated with PS domains wetting the wide PS-attractive stripe. In the center of the film, the domain half-width of all samples is  $(11.6\pm0.1)$  nm, which is the bulk equilibrium dimension. We conclude that interactions at each interface are deforming the domain shapes, and these effects decay with depth into the film interior.

#### **11.3** Self Consistent Mean Field Theory Simulations

To assist in interpretation of SAXS data, we performed two-dimensional SCFT simulations of symmetric *AB* diblock copolymers confined between a hard substrate and a stationary copolymer-air interface, where both the substrate and the air were modeled using fixed "particles" and implemented in the SCFT simulations as a fixed particle field or masking field [121]. Details of the SCFT framework used here can be found in numerous recent publications [121–123]; here we provide a brief summary of the most salient features.

The substrate-copolymer interface was modeled as a relatively diffuse gradient between the pure particle/substrate phase and the pure copolymer melt phase. The interfacial region was approximately 3 nm wide, corresponding to a brush layer that allows for significant copolymer penetration. The substrate was defined to have two different chemical selectivities, consistent with the chemically patterned substrate in the real PS-PMMA films. The air-polymer interface was modeled using a slightly sharper copolymer gradient with a width of approximately 1.4 nm. With these definitions, there were four independent model parameters,  $\chi N$ ,  $\chi_{PS}N$ ,  $\chi_{OPS}N$ , and  $\chi_{air}N$ . Here N is the index of polymerization;  $\chi$  is the A-B Flory parameter; and  $\chi_{PS}$ ,  $\chi_{OPS}$ , and  $\chi_{air}$  are composite Flory parameters for the AB copolymer and the PS brush, the partially oxidized PS brush, and the air interface, respectively. The composite Flory parameter for the PS brush is defined such that  $\chi_{PS} = (\chi_{PS,A} - \chi_{PS,B})/2$ , where  $\chi_{PS,A}$  is the Flory parameter for the PS brush and the A segments, and  $\chi_{PS,B}$  is the Flory parameter for the PS brush and the B segments. There are similar definitions for  $\chi_{OPS}$  and  $\chi_{air}$ . Positive values of the composite Flory parameters indicate an energetic propensity to prefer B segments, while negative values indicate an energetic propensity to prefer A segments.

For all simulations,  $\chi N = 38$ . This value of  $\chi N$  is consistent with the previous work [107]. The value of  $\chi_{air}N$  was selected to be  $\chi_{air}N = 0$  or  $\chi_{air}N = -3.8$ , consistent with an air interface that is neutral or slightly preferential towards A segments, respectively. Therefore, one can identify the A segments in the simulations with the PS segments in the real BCP film. The values of  $\chi_{PS}N$  and  $\chi_{OPS}N$  were selected in order to capture the effects of the substrate-BCP interactions. Accordingly,  $\chi_{PS,A}N = 0$  and  $\chi_{PS,B}N = 38$ , while we set  $\chi_{OPS,A}N = 38$  and  $\chi_{OPS,B}N = -38$ ; thus, we have  $\chi_{PS}N = -19$  and  $\chi_{OPS}N = 38$ .

The equilibrium pitch of the AB BCP was determined to be  $L_0 = 2\pi/k_0 \approx 4.7R_g$ , where  $R_g$  is the BCP radius of gyration, and  $k_0$  is the location of the primary peak in the simulated structure factor  $S(k) \propto |\phi_{\mathbf{k}}|^2$ . The equilibrium pitch of the BCP was calculated using a *bulk* SCFT simulation with  $\chi N = 38$ . The simulation space was defined to be approximately one unit cell wide, so that  $L_x = 4.7R_g \approx L_0$ . The film thickness was selected to be  $L_y \approx 1.4L_0 = 6.58R_g$ , consistent with the real BCP film. Finally, the spatial resolution for the SCFT simulations was  $\Delta x = \Delta y \approx 0.04R_g$ with  $2^5 = 32$  points along the copolymer backbone. The SCFT relaxation process also requires defining an effective "time step" for both the pressure and exchange field relaxations [122]. In all SCFT simulations, we used  $\Delta t = 4$ . The pressure field was updated using a first-order accurate, explicit Euler method, and the exchange field was updated using a first-order accurate, semi-implicit Euler method.

Figure 11.3(c-d) reports the simulations for PS domains assembled on a PSattractive stripe with dimensions  $w_{PS} = 0.7L_0$ . The simulated domain shape agrees qualitatively with experimental data and captures the large "foot." This feature is potentially explained by the diffuse brush-copolymer interface. The copolymer penetrates the brush layer resulting in an A-B interface with a pronounced "foot" or splay at the substrate. This is clear in the SCFT simulations, and it could explain the large foot predicted by the SAXS fits. We note that several experimental works have demonstrated that copolymer domains can penetrate an underlying brush and interact with an underlying substrate |124-126|. While not presented here, we tested this hypothesis by simulating a similar BCP cross section with a much sharper copolymer-substrate interface. In this scenario, a pronounced foot was not observed because significant copolymer penetration into the brush layer was not possible. The SCFT simulations do not predict significant rounding of the domain shape near the copolymer-air interface, yet this feature is needed to fit experimental spectra. We speculate that the top-rounding is due to swelling of the PMMA domain by ambient humidity [126], which is consistent with the atomic force microscopy height measurement in 11.1 (where PMMA domains are slightly "taller" than PS).

The apparent interfacial width is a convolution of the mean-field composition profile and thermal fluctuations, which is discussed extensively elsewhere [105, 106, 127]. The values extracted for each sample were  $(4.90 \pm 0.02)$  nm,  $(4.95 \pm 0.02)$  nm,  $(4.80\pm0.02)$  nm, and  $(4.90\pm0.02)$  nm, which are very consistent with prior predictions and measurements for the same PS-PMMA lamellar copolymer [107]. The apparent interfacial width contains information about line-edge roughness, an important metric for semiconductor manufacturing that refers to low-frequency variations in the lineedge position. Ultimately, we intend to extract the line-edge roughness spectrum from the scattering data, as specific frequency ranges have markedly different effects on final device function [128]. Armed with a physically reasonable model for fluctuations and line-edge roughness [105, 106, 129–133], we hope to extract the spectral information from the diffuse scattering around the diffraction peaks in the  $q_y$  direction.

# Chapter 12 Conclusions and Outlook

## 12.1 Conclusions

In order to accurately determine the kinetic and the transport parameters we examined the acid-catalyzed deprotection of our model glassy polymer resin with infrared absorbance spectroscopy and stochastic simulations. We interpreted experimental data with a model that explicitly accounts for acid transport, but local heterogeneities are introduced through a non-exponential distribution of waiting times between successive hopping events. The anomalous diffusion can be visualized as a hopping process with binding-unbinding events at energetic traps [45]. We find that subdiffusive behavior with long-tail kinetics can capture key attributes of the observed deprotection rate, offering a near-quantitative description of macroscopic deprotection rates - and only two parameters need to be specified. The same model parameters can describe the dependence of deprotection level on acid concentration, and their variation with temperature follows the expected behavior. With high acid loadings, we found it necessary to include acid-acid interactions that deplete the effective acid concentration.

We measured the latent chemical image of a model CA resist system with small angle x-ray scattering. The basis for the use of x-ray diffraction techniques for our measurements were the volume reduction, and thus the density change the polymer undergoes at deprotection. We characterized the density change with x-ray reflectivity by measuring the scattering length density of the protected and the deprotected polymers. We modeled the reflectivity using the Parratt approach to calculate the scattering length density. We observed that there is a change in scattering length density with the deprotection reaction. However, we did not observe a trend in this change with post exposure bake temperature in our experimental temperature range.

To measure the depth dependent domains we nanopatterned line gratings of 20  $\mu$ m length and 1.37 nm width on 80 nm thick CA resist films post exposure baked at 90° - 130°C for 10, 15 and 20 seconds. These samples were measured in variable incidence small angle x-ray scattering. We modeled the scattering data using an inverse calculation method, to calculate the depth dependant domain shape and the width of the deprotection interface. We found that the image resolution varies with the distance from the free surface and the substrate. We attribute the above result to the free surface and the substrate interactions. It was difficult to characterize the thermal attributes of the copolymer due to thermal instability which made the glass transition temperature measurements challenging. However from the measurements taken at a 100 nm and a 32 nm films it could be observed that there was a slight increase in the glass transition temperature with the reduction in film thickness. This may indicate the presence of polymer-substrate interactions. Simulations reveal that the origins of depth dependent deprotection levels is due to depth-dependent diffusion rates and a surface excess of acid catalyst. In addition, we understand that enhanced acid diffusivity at the free surface will also generate a broader deprotection interface.

We used a similar approach to measure the cross-sectional shape of PS-PMMA line gratings. The experimental data were interpreted with the aid of numerical simulations based on SCFT. The concerted experimental and modeling effort demonstrates that DSA pattern quality is strongly affected by the types of interactions at each interfaces. Specifically, we measured a relatively large "foot" at the copolymer– substrate interface that results in a subtle "neck" and "shoulder" in the grating cross section. SCFT simulations corroborate this observation and suggest that the foot is a result of significant copolymer penetration into the underlying brush layer. These observations are important for lithography scientists because vertical domain sidewalls are needed for optimal pattern transfer. Significantly, these findings suggest that new coatings for DSA should consider copolymer penetration lengths in addition to tailoring surface energetics.

#### 12.2 Outlook

In general, the measurement, characterization, and inspection of 10 nm features poses a significant challenge. Traditional microscopy techniques are unreliable because they examine a small subset of the entire sample, are most sensitive to the sample surface, and have established resolution problems at the 10 nm scale. Optical methods such as scatterometry need *validated* measurement libraries for data analysis, so it is difficult to extend these metrologies to new materials and processes. On the other hand, transmission SAXS can resolve the full three-dimensional shape of periodic nanopatterns with high spatial resolution (e.g., < 1 nm). Furthermore, SAXS is an *ensemble-averaged* measurement, so meaningful statistical information can be extracted from these data without the need for numerous repeat experiments. Synchrotron X-ray scattering has the potential to emerge as a "gold-standard" or "benchmark" dimensional metrology and library validation tool for high density, sub-10 nm features.

The technique and the developed quantitative models can be applied to any CA resist exposed to a periodic pattern. Being able to directly measure the latent image aids in rapid screening of new materials and also enables the development of predictive, quantitative models. X-ray diffraction combined with quantitative modeling provides the feedback to lithographic patterning processes.

Free surface and the polymer-substrate interactions gives rise to non-uniform free volume distribution through the depth of the polymer film. Diffusion lengths can be controlled by tuning interfacial interactions. An interfacial layer such as a selfassembled monolayer between the substrate and the resist film, the polymer-substrate interactions can be modified. Coating a polymer on top of the free surface of the resist would restrict the polymer motion in post exposure bake, restricting the free volume generation. Being able to measure the image resolution incorporating each of these factors allows to better understand the effect surface and interfacial phenomena in resist gratings.

The local randomness in the positions of acids generated by the exposure produces line edge roughness (LER) at the interface between the protected and the deprotected polymer. LER is a critical concern with nanoscale lithography [1, 2, 19]. Width of the interface between the protected and the deprotected domains can be calculated by x-ray diffraction measurements which is beneficial to identify the possible reasons and to investigate the effect of each additive to the resist system on LER.

# Chapter 13 Spatial Coherence in Electron-Beam Patterning

# 13.1 Introduction

Electron beam lithography (EBL) is a maskless technology for patterning at the nanoscale that is popular for research, development, and manufacturing of nanostructured devices. EBL patterns a radiation-sensitive film called a "resist" by scanning a tightly-focused electron beam across the surface of the sample. This serial exposure process is illustrated in Figure 13.1, where the circles denote each "pixel" exposed to the electron beam. The resist solubility is altered by exposure to radiation, so subsequent immersion in a developer selectively removes either the exposed (positive-tone) or unexposed (negative-tone) material. EBL is commonly used for patterning semiconductor devices [134], plasmonic arrays [135], photonic crystals [136], templates for directed assembly [137], and imprint templates [138].



Figure 13.1: Schematic illustrating scanning electron-beam lithography. Each circle marks a pixel addressed by the beam, and each line of legnth L is generated with 6 passes.

Advances in EBL technology have focused on reduction in feature size through system design and resist processing [139], but there have been few efforts to control feature *placement* over large distances. These trends are partly driven by the needs of the semiconductor industry, where local feature overlay is more critical than longrange spatial coherence. However, precise long-range pattern placement is important for micro- and nano-photonic devices that rely on coherent interference effects, and nanoscale variations in critical dimension (pitch) will likely impact the performance of next-generation devices [140]. Electron-beam lithography systems operate with an open-loop control scheme, which means they cannot reference the beam location during an exposure [141, 142]. As such, noise during the exposure will displace the pattern elements from their design positions, and the noise characteristics are difficult to determine with standard diagnostic techniques like scanning electron microscopy (SEM).

We demonstrate that noise during the EBL exposure introduces *periodic* errors in feature placement that are easily detected with transmission x-ray diffraction (XRD) measurements. A simple and accurate model is described to analyze the diffraction data, identify the noise sources, and calculate the resulting variations in pitch. Line gratings were patterned with a 46 nm average pitch using electron-beam lithography. The resist was a 33 nm thick film of poly(methylstyrene-*co*-chloromethyl acrylate), commonly known as ZEP manufactured by Zeon Chemicals, and exposure doses were varied from 950  $\mu$ C/cm<sup>2</sup> up to 1130  $\mu$ C/cm<sup>2</sup>. A representative scanning electron microscopy (SEM) micrograph of a 46 nm pitch line grating is shown in Figure 13.2a. Samples were measured with XRD using synchrotron soft x-ray radiation with wavelength  $\lambda = 4.59$  nm. The diffraction geometry is illustrated in Figure 13.2b. (Note that hard x-ray radiation is also suitable for these experiments, and most systems do not require a synchrotron source for sufficient signal-to-noise.) The diffraction profiles contained numerous "satellite" peaks, meaning weak diffraction peaks adjacent to the



Figure 13.2: (a) Representative SEM measurement of 46 nm pitch line grating with Fourier transform (inset). Resist is ZEP and exposure dose is 950  $\mu$ C/cm<sup>2</sup>; other relevant exposure parameters are summarized in Table 13.1. (b) Transmission x-ray diffraction geometry. (c) Periodic compressions and extensions of the grating pitch characterized by period  $\Lambda = 2\pi/k_x$ . Average pitch is *d* and the standard deviation is  $\sigma \approx d\epsilon$ . (d) Primary diffraction peaks are distributed with periodicity  $q_x = 2\pi n/d$ , where *n* is an integer, and satellite peaks are adjacent to each primary peak at  $\pm k_x = 2\pi/\Lambda$ .

strong primary nodes, that are characteristic of periodic extensions and compressions in the grating pitch. These features are illustrated in Figures 13.2c-d. The wavelength and amplitude of these pitch variations were calculated with a simple scaling law by comparing the intensities and positions of satellite peaks relative to their primary nodes. To identify the noise sources, three samples must be prepared with different write frequencies. Variations in pitch are determined independently for each sample.

XRD is a popular technique for characterizing nanostructured thin films because

it offers better accuracy, resolution, and statistics than microscopy. Quantitative analysis of diffraction data usually requires a complex model for the wave amplitudes: For example, the diffracted intensity from a simple line grating is a function of nanostructure shape, size, periodicity, and edge roughness [71, 107, 109, 111, 143]. However, the methods described in this paper are easy to implement because they do not require any modeling of the diffracted wave amplitudes. Instead, the data are analyzed by fitting peak positions and intensities to a simple scaling law. Measurements must be completed from periodic patterns, such as regular arrays of lines or dots, but there are no other requirements for successful implementation of these methods.

# **13.2** Experimental Procedures

Certain materials and procedures are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the authors or their institutions, nor is it intended to imply that the materials or procedures identified are the best available for the purpose.

Substrate Fabrication XRD experiments require a transparent substrate, so we fabricate all samples on silicon nitride (SiN) membranes that are approximately 50% transparent to 270 eV radiation. A 100 nm thick film of low-stress (silicon rich) SiN is deposited on clean  $\langle 100 \rangle$  silicon wafers using low-pressure chemical vapor deposition with the following parameters:  $7.44 \times 10^{-5}$  moles/sec (100 sccm) dichlorosilane,  $1.49 \times 10^{-5}$  moles/s (20 sccm) ammonia, 33 Pa (250 mT), and 835°C. The deposition rate is 6.9 nm/min, and the film stress is (170 ± 10) MPa tensile. The front side of the substrates is then patterned with gold "alignment marks" that are aligned with the crystallographic axes of the silicon wafer. These marks are used to define the position and orientation of the electron beam lithography patterns, which ensures

the patterned gratings are properly aligned with the x-ray beam. The backside of each wafer is patterned with an array of "windows" where the SiN film is removed with a CHF<sub>3</sub> reactive ion etch. Membranes are created by etching away the silicon in the "window" areas with a 30 wt% potassium hydroxide solution (aqueous) at 40°C for two days. The resulting membranes span 1 mm ×1 mm. The backside of the membranes is then coated with 400 nm of aluminum, which is necessary to ensure a uniform substrate thermal conductivity for spin-casting and bake processes. (Note that aluminum is removed prior to XRD measurements).

Electron beam lithography Substrates were spin coated with a 33 nm thick film of poly(methyl styrene-*co*-chloromethyl acrylate) electron beam resist (ZEP, Zeon Chemicals) and baked at 180°C for two minutes. Line gratings were patterned using an accelerating voltage of 100 keV, beam current of 1.1 nA, and beam step size of 2 nm. The design line width was 12 nm (6-passes), and the design pitch was 46 nm. Exposure dose was varied from 950 to 1130  $\mu$ C/cm<sup>2</sup>. The coherence length of the gratings is determined by the length of the beam deflection, which was set to 16  $\mu$ m. An area of 1 mm ×1 mm was patterned by stitching together 62 gratings that spanned 16  $\mu$ m ×16  $\mu$ m. The ZEP resist was developed in hexyl acetate at -6°C for 40 seconds, followed by a 10 second rinse in isopropyl alcohol and dried in nitrogen. After pattern development, the aluminum coating is rinsed off the back of the membranes using 45 wt% potassium hydroxide solution at room temperature.

**X-ray Diffraction** Transmission x-ray diffraction (XRD) measurements were completed at the Advanced Light Source beam line 6.3.2 using a photon energy of 270 eV ( $\lambda = 4.59$  nm). The scattering geometry is illustrated in Figure 13.2. The sample is illuminated at normal incidence, and the scattering is recorded by scanning a channel electron multiplier detector mounted on a rotating arm from  $2 - 45^{\circ}$  in 0.1° increments. The signal is averaged for 10 seconds per angle. Each diffraction measurement samples an area of 500  $\mu$ m ×300  $\mu$ m, and data were recorded from two locations per sample. The lateral coherence length of the radiation is on the order of a few micrometers. The resist grating axis was aligned to the y-axis with an accuracy of  $\pm 1^{\circ}$ . The elastic scattering vector is  $\mathbf{q} = \mathbf{g}_f - \mathbf{g}_i$ , where  $\mathbf{g}_f$  and  $\mathbf{g}_i$  are the incident and scattered wave vectors, respectively. Correcting for refraction at the polymer interfaces, the wave vectors inside the film are defined as  $\mathbf{g}_i = 2\pi \{\sin \alpha_i, 0, (n_p^2 - \sin^2 \alpha_i)^{0.5}\} / \lambda$ and  $\mathbf{g}_f = 2\pi \{\sin 2\Theta, 0, (n_p^2 - \sin^2 2\Theta)^{0.5}\} / \lambda$ , where  $n_p$  is the refractive index of the polymer film.

## 13.3 Analysis of X-ray Diffraction Data

Our objective is to characterize periodic extensions and compressions in grating pitch that result from noise during electron-beam patterning. This section describes a simple method to measure the wavelength and amplitude of such displacements with x-ray diffraction. Our approach does not require any modeling of the diffracted wave amplitudes: Instead, the calculations are based on comparing the positions and intensities of the primary diffraction peaks with their adjacent "satellites." The following paragraphs briefly introduce the relevant theory and assumptions.

The diffracted intensity from a resist line grating with density profile  $\rho(\mathbf{r})$  is:

$$I(\mathbf{q}) = I_{\rm m}(\vec{q}) + I_{\rm d}(\mathbf{q}) = |\langle \tilde{\varrho}(\mathbf{q}) \rangle|^2 + \langle |\tilde{\varrho}(\mathbf{q}) - \langle \tilde{\varrho}(\mathbf{q}) \rangle|^2 \rangle.$$
(13.1)

Note that  $\tilde{\varrho}(\mathbf{q})$  is the Fourier transform of  $\rho(\mathbf{r})$ ,  $\mathbf{r} = \{x, y, z\}$  is the real-space position vector, and  $\mathbf{q} = \{q_x, q_y, q_x\}$  is the scattering vector.  $I_m(\mathbf{q})$  is the scattering from the mean density profile, and reflects the average pitch, line width, sidewall angle, and line-edge roughness of the gratings across the sampled area.  $I_d(\mathbf{q})$  is the diffuse scattering from concentration defects or lattice disorder. In general, diffuse scattering is difficult to distinguish from background noise in the measurement. However, *periodic* displacements in the grating pitch produce weak satellite peaks that are easily identified in the diffraction data [144]. Primary and satellite peaks are shown in Figures 13.2 and 13.3.



Figure 13.3: Comparison of XRD data and SEM Fourier transforms. (a,b) Diffraction data from two different ZEP resist gratings and fits to the scaling law in Equation (13.5). (c) Enlarged region of (b) that shows primary diffraction peaks along with two satellites at  $k_{x,1} = 2\pi/\Lambda_1$  and  $k_{x,2} = 2\pi/\Lambda_2$ . Satellites marked "1" and "2" are associated with noise frequencies ( $62 \pm 2$ ) Hz and ( $86 \pm 3$ ) Hz, respectively. A third satellite peak associated with ca. 150 Hz noise is visible in these data but was not detected in every sample. (d,e) Fourier transforms of SEM data from two different ZEP resist gratings and fits to the scaling law in Equation (13.5). (f) Enlarged region of (e) shows primary diffraction peaks along with the two satellites. SEM data are significantly noisier than XRD and do not agree with the  $q^2$ -scaling law.

The mean density profile  $\langle \rho(\mathbf{r}) \rangle$  is modeled by convolving a one-dimensional lattice  $\delta_n(x - nd)$  with a function  $s(\mathbf{r})$  that describes the average size, shape, and

line-edge roughness of the gratings. The mean diffracted intensity is:

$$I_{\rm m}(\mathbf{q}) = \sum_{n=-\infty}^{n=\infty} \delta(q_x - 2\pi n/d) \cdot |\widetilde{s}(\mathbf{q})|^2 \cdot |\widetilde{h}(\mathbf{q})|^2.$$
(13.2)

Diffraction from the mean density profile is observed at discrete positions  $q_{x,n} = 2\pi n/d$ , and we refer to these features as the *primary peaks*. The function  $|\tilde{s}(\mathbf{q})|^2$  is the "form factor," and describes the shape of the resist cross-section. The function  $|\tilde{h}(\mathbf{q})|^2$  describes the attenuation of the diffraction signal due to line-edge roughness.

The diffuse scattering from periodic changes in pitch is described by Guinier: [144] Displacements in the grating pitch at a point  $x_n$  are described by the wave  $\Delta \mathbf{x}_n = \mathbf{A} \cos(\mathbf{k}.\mathbf{x}_n)$ , where  $\mathbf{A}(=\epsilon/k_x)$  is the amplitude and  $\mathbf{k}$  is the propagation vector. The grating pitch then varies sinusoidally from  $d(1-\epsilon)$  to  $d(1+\epsilon)$ , which is illustrated in Figure 13.2(b). If the amplitudes of the displacements are small, i.e.,  $\epsilon \ll 1$ , then the scattering from the mean density profile I<sub>m</sub> and the diffuse scattering from the satellites I<sub>sat</sub> are:

$$I_{\rm m}(\mathbf{q}) = I(\mathbf{q}) \left\{ 1 - q_{\rm x}^2 \epsilon^2 k_{\rm x}^{-2} / 4 \right\}, \tag{13.3}$$

$$I_{sat}(\mathbf{q}) = I(\mathbf{q} \pm \mathbf{k}) \{ q_x^2 \epsilon^2 k_x^{-2} / 4 \}.$$
 (13.4)

The satellite peaks in the resist data are positioned adjacent to the primary nodes at  $q_x \pm k_x$ . Note: Detailed derivation of equations (13.24) and (13.25) is illustrated in Section 13.6

#### 13.3.1 Noise Amplitudes

The scaling law described by Equation (13.5) provides a simple method to calculate  $\epsilon$  from the relative intensity of satellite to primary peaks, eliminating the need for complex models to describe resist sidewall angle, line-edge roughness, and size polydispersity. The scaling law is derived from Equations (13.24)-(13.25) using two approximations: First, if the form factor does not sharply vary near the primary peaks, we can write  $|\tilde{s}(\mathbf{q})|^2 \simeq |\tilde{s}(\mathbf{q} \pm \mathbf{k})|^2$ . This approximation is valid if the positions of primary peaks do not coincide with minima in the form factor. Second, we note that line-edge roughness slowly damps the intensity with increasing  $q_x$ , so the approximation  $|\tilde{h}(\mathbf{q})|^2 \simeq |\tilde{h}(\mathbf{q} \pm \mathbf{k})|^2$  is always valid. These simplifications lead to the following result:

$$I_{\text{sat}}/I_{\text{m}} \simeq q_{\text{x}}^2 \epsilon^2 / 4k_{\text{x}}^2. \tag{13.5}$$

The Results and Discussion section includes a comparison between the simple scaling law described by Equation (13.5) and diffraction models that include the wave amplitudes according to Equations (13.24)-(13.25). The results are identical within experimental error.

#### 13.3.2 Noise Frequencies

Our objective is to identify the noise sources that produce pattern placement errors in the electron beam lithography exposure. The noise frequency  $\omega_n$  is calculated from the number of lines per noise cycle  $(\Lambda/d)$  and the time required to expose each line (the speed of the pattern generator). Note that  $\Lambda$  is measured from the XRD data, while the following parameters are specified by the exposure conditions: Grating pitch d, area dose, beam current c, beam step size p, line length L, and the number of passes per line  $N_p$ ,

$$\frac{1}{\omega_i} = \frac{\text{lines}}{\text{cycle}} \times \frac{\text{steps}}{\text{line}} \times \frac{\text{time}}{\text{step}} = \frac{\Lambda}{d} \times \frac{N_p \times L}{p} \times \frac{\text{dose} \times p^2}{c}.$$
 (13.6)

The Results and Discussion section includes XRD measurements from nanoscale line gratings exposed at different doses while all other conditions were held constant. We expect to see  $\Lambda/d$  scale with exposure dose as follows:

$$\frac{\Lambda}{d} = \frac{1}{\omega_i} \times \frac{c}{N_p \times L \times p} \times \frac{1}{\text{dose}}.$$
(13.7)

The noise frequency  $\omega_i$  can then be calculated from a plot of  $\Lambda/d$  vs. dose.

$$\frac{\text{time}}{\text{line}} = \frac{\text{steps}}{\text{line}} \times \frac{\text{time}}{\text{step}} = \frac{N_p \times L}{p} \times \frac{I}{\text{dose} \times p^2}.$$
(13.8)

The wavelength of periodic extensions and compressions in the grating pitch of displacements cycles calculated from the satellite peak positions in the x-ray diffraction profile can be used to determine the background noise frequencies which were present at the time of e-beam exposure of the samples, using equation (13.7).

$$\frac{\Lambda}{d} = \frac{\omega_{exp}}{\omega_{n}} \times \left(\frac{\text{pixels}}{\text{line}}\right)^{-1},\tag{13.9}$$

where  $\omega_{exp}$  and  $\omega_n$  are exposure and noise frequencies respectively.

#### 13.4 Results and Discussion

Line gratings with a d = 46 nm pitch were patterned at four exposure doses: 950, 1010, 1070, and 1130  $\mu$ C/cm<sup>2</sup>. All other exposure parameters were the same for each sample, and are listed in Table 13.1. Representative XRD data are shown in Figures 13.3(a)-13.3(b). Two distinct satellite peaks were always observed in the diffraction data, which indicates that two persistent noise sources were present during the electron-beam patterning. These two satellites are visible in Figure 13.3(c).

Three methods of analysis were used to determine the primary peak positions

Table 13.1: Summary of e-beam parameters used to pattern the line gratings. Gratings for XRD span a total area of 1 mm  $\times$  1 mm (62 smaller gratings spanning 16  $\mu$ m  $\times$  16  $\mu$ m are stitched together). Gratings for SEM spanned 100  $\mu$ m  $\times$  100  $\mu$ m.

Parameter	Value
Grating pitch $(d)$	46  nm
Beam current $(c)$	1.1 nA
Area exposure dose (dose)	950-1310 $\mu C/cm^2$
EBL pixel size $(p)$	2 nm
Passes per line $(N_p)$	6
Line length $(L)$	$16 \ \mu m$

 $q_{x,n}$ , satellite positions  $q_{x,n}\pm k_{x,i}$ , primary amplitudes  $I_{\rm m}(q_{x,n})$ , and satellite amplitudes  $I_{\rm sat}(q_{x,n}\pm k_{x,i})$  from each data set. The parameters  $k_{x,i}$  are the frequencies of periodic extensions and compressions in the pitch, and are needed to identify the noise sources using Equation 13.7. The parameters  $q_{x,n}$ ,  $k_{x,i}$ ,  $I_{\rm m}(q_{x,n})$ , and  $I_{\rm sat}(q_{x,n}\pm k_{x,i})$  are all needed to calculate  $\epsilon$  by Equation 13.5. Note that the standard deviation in the grating pitch is  $\sigma \simeq d\epsilon$ . The three methods for diffraction data analysis are as follows:

- 1. Satellite amplitudes and positions were obtained by visual inspection of the diffraction data. A "point-and-click" algorithm was implemented in Matlab where the user identified each peak by visual inspection. The parameter  $\epsilon$  is then calculated for each set of diffraction data using Equation (13.5). The noise frequencies are determined with Equation (13.7), which requires the noise wavelengths  $\lambda_i = 2\pi/k_{x,i}$ as a function of exposure dose (Figure 13.4).
- 2. Peak positions and amplitudes were fit with an automated routine based on the  $q^2$ -scaling law of Equation (13.5). The "point-and-click" algorithm is used to acquire initial guesses for peak positions and amplitudes. The software fits a Gaussian function to each primary peak to calculate the amplitude  $I_m(q_x)$  and

position  $q_x$ . The software automatically detects the positions of adjacent satellites  $q_x \pm k_x$  and fits the satellites to a Gaussian function, where the Gaussian peak amplitude  $I_{\text{sat}}(q_x \pm k_x)$  is constrained according to the scaling law of Equation 13.5. Regression analysis uses  $\epsilon$  as an adjustable parameter. Representative experimental data are shown in Figures 13.3(a)-(c) with fits to the  $q^2$ -scaling law.

3. For comparison, diffraction data were fit using the models described by Equations 13.2-13.25. This approach calculates the peak intensities as a function of the size, shape, and line-edge roughness of the resist patterns. Full details are provided elsewhere [107].



Figure 13.4: Noise cycles  $\Lambda/d$  for each satellite peak as a function of EBL exposure dose. Solid lines are fits to Equation 13.7. (a) XRD results. The noise frequencies calculated from visual inspection (red), scaling law (green), and the scaling law with form factor corrections (blue) all closely agree. Error bars represent the uncertainty in determining  $k_x = 2\pi/\Lambda$  from the diffraction data, which is 0.001 nm<sup>-1</sup> by any method. (b) SEM results. Noise frequencies are calculated from visual inspection; other algorithms fail due to SEM image artifacts. Each data point represents the average value of  $k_x$  measured from each image and error bars encompass  $\pm 1$  standard deviation.



Figure 13.5: Analysis of ca. 62 Hz and 86 Hz noise in a grating exposed at 950  $\mu$ C/cm<sup>2</sup>. (a,b) XRD data were analyzed with the "point-andclick" algorithm based on visual inspection. Line is the best fit, and the best-fit slope for both data sets is  $2.0 \pm 0.1$ . This is the slope predicted by the scaling law established with Equation (13.5). (c) SEM data were analyzed with the algorithm based on visual inspection, but results do not follow the scaling predicted by Equation (13.5).

The first objective is to identify the noise frequencies  $\omega_i$  from the dependence of  $\Lambda_i/d$  on exposure dose, i.e., the relationship predicted by Equation (13.7). These noise characteristics were determined by fitting  $\Lambda_i$  vs. exposure dose to Equation (13.7), where the noise frequency  $\omega_i$  was an adjustable parameter for linear regression. The results are shown in Figure 13.5. Red, blue, and green curves correspond with analysis methods 1, 2, and 3, respectively. The two noise frequencies determined with Equation (13.7) are  $\omega_1 = (62 \pm 2)$  Hz and  $\omega_1 = (86 \pm 3)$  Hz, and the results from each method of data analysis agree within experimental error. All laboratory equipment runs on 60 Hz mains power, so the ~ 60 Hz noise is likely electromagnetic in nature. A vibrating component within the electron-beam exposure tool was identified as the source of the ~ 86 Hz noise [145]. Note that noise frequencies ranging from 150 Hz to 175 Hz were occasionally detected in the diffraction data, but the sources were intermittant and could not be identified.

The second objective of the data analysis is to calculate the standard deviation in the grating pitch using the  $q^2$ -scaling proposed in Equation 13.5. To validate the scaling law, we note that figures 13.3(a)-(b) show good agreement between the diffraction data and fits to the  $q^2$ -scaling law. Furthermore, peak detection through visual inspection confirms the scaling: The peak positions and amplitudes were detected with the "point-and-click" algorithm, and plots of  $\log(I_{\text{sat}}k_x^2/I_m)$  vs.  $\log(q_x)$ were prepared for the  $\sim 60$  Hz and  $\sim 86$  Hz satellite peaks. Examples of these data are shown in Figure 13.5 for a grating exposed at 950  $\mu C/cm^2$ . The gradient of the plot is equal to  $2.0 \pm 0.1$ , which is the value predicted by the scaling law in Equation 13.5. The y-intercept of the linear-fit curve gives the fractional variation in grating pitch ( $\epsilon$ ) with respect to the design value of 46 nm. The standard deviation in the grating pitch is  $\sigma \simeq d\epsilon$ . The semiconductor industry quotes line width and overlay tolerances in terms of  $3\sigma$ , so results for  $3\sigma$  as a function of exposure dose are shown in Figure 13.6. Note that red, blue, and green data points were acquired with analysis methods 1, 2, and 3, respectively. The  $3\sigma$  values for each noise frequency range from 1.5 nm to 2.5 nm, which is significant in the context of semiconductor manufacturing requirements: More than 4 different "critical" exposures are required to pattern an integrated circuit, so if there is an approximately 50% probability that each step in the process introduces an error of  $\sim 1$  nm, then it will be difficult to achieve overlay with nanometer precision. These errors are also significant for photonic devices, where nanoscale variations can impact the coupling efficiencies, cavity quality factors, and center wavelength values [135, 136, 146].



Figure 13.6: The  $3\sigma$  variation in grating pitch as a function of EBL exposure dose, where  $\sigma$  is the standard deviation. Open and closed symbols correspond with ca. 62 Hz and 86 Hz noise, respectively. (a) XRD data analysis. Calculations based on visual inspection (red), scaling law (green), and the scaling law with form factor corrections (blue) all closely agree. Note that 86 Hz noise (mechanical) exhibits greater variation between samples than the 62 Hz noise (electromagnetic). (b) SEM data analysis with the scaling law. Calculated standard deviations are consistent with XRD analysis despite poor agreement between SEM data and the scaling law.

The noise frequencies that can be identified with diffraction are determined by both the resolution of the diffraction experiment and the design parameters of the grating. The observable frequency limits at each exposure dose for our 46 nm pitch

Table 13.2: Minimum  $(\omega_{min})$  and maximum  $(\omega_{min})$  noise frequencies that are detectable at each exposure dose. Note that these limits are calculated for the specific experimental conditions outlined in the paper, and other frequency ranges are accessible by adjusting the exposure parameters.

Dose $(\mu C/cm^2)$	$\omega_{min} \ { m XRD}/{ m SEM} \ ({ m Hz})$	$\omega_{max} \text{ XRD/SEM (Hz)}$
950	26/17	554/562
1010	26/16	517/526
1070	24/15	488/496
1130	23/14	465/473

gratings are listed in Table 13.2, and range from (approximately) 25 Hz to 500 Hz. The minimum and maximum values of  $k_x$  that can be detected were determined as follows: The minimum  $k_x$  value is the closest satellite peak position that can be distinguished from the primary peak. The maximum  $k_x$  value is the satellite peak position that is farthest from the associated primary peak but can be distinguished from neighboring primary peaks (i.e.,  $k_x < 2\pi/d$ ). The minimum/maximum noise frequencies that can be detected were then calculated using equation 13.7.

Last, we note that directed self-assembly with block copolymer resists does not heal these variations in pitch because the chains can stretch or compress to accommodate slight perturbations [107]. However, once the frequencies of noise sources are identified, it should be feasible to design algorithms that minimize errors in feature placement.

#### 13.5 Conclusions

Periodic noise during an electron beam lithography exposure can displace the pattern elements from a perfect grid. We present a simple method to measure the wavelength and amplitude of these displacements with transmission x-ray diffraction. Periodic extensions and compressions in the lattice produce "satellites" that are adjacent to the primary diffraction peaks. The wavelength and amplitude of the displacement wave are calculated by comparing the intensities and positions of satellite peaks relative to the primary nodes. Two persistent noise frequencies were identified,  $(60 \pm 2)$  Hz and  $(86 \pm 2)$  Hz, and occasionally frequencies in the range of 150 Hz to 175 Hz were also observed. These experiments can detect noise in the range of 25 Hz to 500 Hz, and the exposure parameters (grating pitch, exposure frequency, etc.) could be changed to probe different limits. The 60 Hz and 86 Hz noise produce errors in a 46 nm grating pitch of  $3\sigma = 1$  nm to 2 nm, where  $\sigma$  is the standard deviation in the grating pitch. These errors are significant in the context of requirements for next-generation lithography, photonic crystals, and plasmonic devices.

## 13.6 Amplitude of the Noise Peaks : Derivation

Assume the atom situated at the node  $\mathbf{x}_n$  is displaced from this node by a distance

$$\Delta \mathbf{x}_n = \mathbf{A} \ \cos \left( \mathbf{k} \cdot \mathbf{x}_n \right), \tag{13.10}$$

where  $\mathbf{A} \ (= \epsilon/k_x)$  is the amplitude and  $\mathbf{k}$  is the propagation vector. The nodes at which the vibrations are in phase are distributed in planes such that  $\mathbf{k}.\mathbf{x}_n$  is constant, indicating that the wavefronts are normal to  $\mathbf{k}$ . The minimum distance between two planes where the phase is the same, or the wavelength of the satellite peak is given by  $\Lambda = 2\pi/|\mathbf{k}|$ . The grating pitch then varies sinusoidally from  $d(1-\epsilon)$  to  $d(1+\epsilon)$ which is depicted in Figure 6(a).

At a given moment, the displacements of the various atoms are statistically identical to those of a given atom at N times separated by intervals which are large with respect to the period of vibration. If atoms are all identical and simply displaced,

$$\mathbf{F}_{n} = \mathbf{F} \, \mathbf{e}^{(-\mathbf{i}\mathbf{q}.\Delta\mathbf{x}_{n})}.\tag{13.11}$$

Since the displacements are small, and the origin of  $\Delta \mathbf{x}_n$  is the average position of the domain, we can simplify the average structure factor as,

$$\bar{\mathbf{F}} = \mathbf{F} \ \overline{\mathbf{e}^{(-\mathbf{i}\mathbf{q}.\Delta \ \mathbf{x}_n)}} = \mathbf{F} \ (1 - \frac{q^2}{2}\Delta \mathbf{x}_n^2). \tag{13.12}$$

We set,

$$\mathbf{F}_{\mathbf{n}} = \bar{\mathbf{F}} + \varphi_{\mathbf{n}}, \tag{13.13}$$

$$\Phi_{\rm m} = \overline{\varphi_{\rm m}} \varphi_{\rm m+n}^*. \tag{13.14}$$

Therefore,

$$\varphi_{n}\varphi_{n+m}^{*} = F^{2} \left[ e^{(-i\mathbf{q}.\Delta\mathbf{x}_{n})} - 1 + \frac{q^{2}}{2}\Delta x_{n}^{2} \right] \left[ e^{(i\mathbf{q}.\Delta\mathbf{x}_{n+m})} - 1 + \frac{q^{2}}{2}\Delta x_{n}^{2} \right], \quad (13.15)$$

which simplifies to,

$$\varphi_n \varphi_{n+m}^* \simeq \mathbf{F}^2 \left[ e^{(-i\mathbf{q}.\Delta \mathbf{x}_n)} - 1 \right] \left[ e^{(i\mathbf{q}.\Delta \mathbf{x}_{n+m})} - 1 \right] \right]. \tag{13.16}$$

Substituting  $\Delta \mathbf{x}_n$  would result in,

$$\varphi_n \varphi_{n+m}^* \simeq \mathbf{F}^2 \left[ e^{(-i\mathbf{q}.\mathbf{A} \cos(\mathbf{k}.\mathbf{x}_n)-1)} \right] \left[ e^{(i\mathbf{q}.\mathbf{A} \cos(\mathbf{k}.\mathbf{x}_{n+m})-1)} \right].$$
(13.17)

Expanding the cosine terms and neglecting higher orders,

$$\varphi_n \varphi_{n+m}^* \simeq \mathbf{F}^2 \ (q.A)^2 \ [\cos(\mathbf{k}.\mathbf{x}_n) \ \cos(\mathbf{k}.\mathbf{x}_{n+m})].$$
 (13.18)

Let,  $\mathbf{x}_{n+m} = \mathbf{x}_n + \mathbf{x}_m$  where  $\mathbf{x}_m$  is a vector in the crystal lattice.

$$\varphi_n \varphi_{n+m}^* = \mathbf{F}^2 (\mathbf{q}.\mathbf{A})^2 \left[ \cos(\mathbf{k}.\mathbf{x}_n) \cos(\mathbf{k}.(\mathbf{x}_n + \mathbf{x}_m)) \right]$$
(13.19)  
$$= \mathbf{F}^2 \frac{(\mathbf{q}.\mathbf{A})^2}{2} \left[ \cos(\mathbf{k}.\mathbf{x}_m) + \cos(\mathbf{k}.(2\mathbf{x}_n + \mathbf{x}_m)) \right].$$

Averaging over all values of n gives,

$$\overline{\varphi_n \varphi_{n+m}^*} = \mathbf{F}^2 \ \frac{(\mathbf{q}.\mathbf{A})^2}{2} \ \cos(\mathbf{k}.\mathbf{x}_m) = \Phi_m. \tag{13.20}$$

According to Equation 13.1,

$$\mathbf{I}(\mathbf{q}) = \mathbf{I}_m(\mathbf{q}) + \mathbf{I}_d(\mathbf{q}), \tag{13.21}$$

$$I_{d}(\mathbf{q}) = F^{2} \Sigma V(\mathbf{x}_{m}) \exp(i\mathbf{q}.\mathbf{x}_{m}), \qquad (13.22)$$

$$I_{d}(\mathbf{q}) = F^{2} \frac{(\mathbf{q}.\mathbf{A})^{2}}{2} \Sigma V(\mathbf{x}_{m}) \cos(\mathbf{k}.\mathbf{x}_{m}) e^{(i\mathbf{q}.\mathbf{x}_{m})}$$

$$= F^{2} \frac{(q.(\epsilon/\mathbf{k}_{x}))^{2}}{4} \Sigma V(\mathbf{x}_{m}) e^{(i(\mathbf{k}+\mathbf{q}).\mathbf{x}_{m})}.$$
(13.23)
If the amplitudes of the displacements are small, i.e.,  $\epsilon \ll 1$ , then the scattering from the mean density profile  $I_m$  and the diffuse scattering from the satellites  $I_{d,sat}$ are:

$$I_{\rm m}(\mathbf{q}) = I(\mathbf{q}) \left\{ 1 - q_x^2 \epsilon^2 k_x^{-2} / 4 \right\}, \qquad (13.24)$$

$$\mathbf{I}_{\text{sat}}(\mathbf{q}) = \mathbf{I}(\mathbf{q} \pm \mathbf{k}) \left\{ q_x^2 \epsilon^2 k_x^{-2} / 4 \right\}, \qquad (13.25)$$

which gives  $I_{d,sat}/I_m \simeq q_x^2 \epsilon^2/4k_x^2$ . The satellite peaks which obeyed the scaling law  $I_{d,sat}/I_m \sim q_x^2$  were then identified as noise peaks.

Table 13.3:	Notation for	models	described	$\mathbf{b}\mathbf{y}$	Equations	$\mathbf{in}$	Chapter
13.							

	4			
$\mathbf{q}$	Scattering vector, $nm^{-1}$			
d	Grating pitch, nm			
Λ	Noise wavelength, nm			
k	Noise propagation vector, $nm^{-1}$			
$\epsilon$	Fractional variation in grating pitch			
ω	Noise frequency, Hz			
C	Beam current, $\mu A$			
dose	Area exposure dose, $\mu C/cm^2$			
p	EBL pixel size, cm			
$N_p$	Number of passes per line			
L	Line length, cm			

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