# ACID TRANSPORT IN CHEMICALLY AMPLIFIED PHOTORESISTS

A Thesis

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 Abhijit Patil

> > > May 2015

# ACID TRANSPORT IN CHEMICALLY AMPLIFIED

## PHOTORESISTS

Abhijit Patil

Approved:

Chair of the Committee Gila E. Stein, Assistant Professor, Chemical and Biomolecular Engineering.

Committee Members:

Vemuri Balakotaiah, Professor, Chemical and Biomolecular Engineering.

Michael P. Harold, Professor, Chemical and Biomolecular Engineering.

Paul Ruchhoeft, Associate Professor, Electrical and Computer Engineering.

Steven Baldelli, Professor, Department of Chemistry.

Suresh K. Khator, Associate Dean, Cullen College of Engineering Michael P. Harold, Professor and Chair, Chemical and Biomolecular Engineering

## Acknowledgements

First, I would like to thank my advisor, Dr. Stein for her support, guidance, and motivation throughout my PhD. Her outstanding mentorship along with her dedication, enthusiasm, patience, and encouragement made this journey a fruitful and pleasant learning experience.

I also want to thank my dissertation committee members Professors Harold, Balakotaiah, Ruchhoeft, and Baldelli for their feedback and questions that made me think and dig deeper into my research. I thank Ginusha Perera, my predecessor on this project. I owe debt of gratitude to my friend Ginusha for showing me the way forward on this project. Special thanks must go to our collaborators on the simulation side, Dr. Manolis Doxastakis and Yogendra Pandey.

Entire Stein group has been a tremendous resource and I thank them all, past and present, collectively. They are Suchanun Moungthai, Nikhila Mahadevapuram, Indranil Mitra, Saeed Ahmadi Vaselabadi, David Truong, Adeline Mah, and Minal Lahoti. I also had privilege of working with Xidong Lin, a graduate student from Chemistry department. I would like to thank Mukund Kabra, a highschool student from Dallas, who worked under me and performed some of the experiments over a summer. Special thanks to Dr. Long Chang and other staff at UH Nanofabrication facility for training me on various instruments.

Finally, I would like to mention and thank my late mother, Shobha, who has been a source of motivation for me through thick and thin and my father, Ashok, and my sister, Shweta, for putting up with, taking care of, and supporting me throughout my career.

# ACID TRANSPORT IN CHEMICALLY AMPLIFIED PHOTORESISTS

An Abstract

of a

Thesis

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 Abhijit Patil

> > > May 2015

## Abstract

Chemically amplified resists (CARs) are a class of lithographic materials that enable high-throughput semiconductor patterning. CARs are comprised of a glassy polymer resin (reactant) loaded with a photoacid generator (inactive catalyst). Patterns are formed by locally activating a strong acid catalyst with light, and then heating the film to promote catalyst diffusion coupled to polymer deprotection. While CARs have been studied for more than 40 years, there are no quantitative models that predict spatial extent of reaction with nanoscale resolution. This poses a significant roadblock for materials design and optimization, as next generation manufacturing processes will target sub-10 nm feature sizes.

We studied reaction kinetics in a model CAR using infrared absorbance spectroscopy and spatially-resolved stochastic simulations. CAR formulas were based on poly(4-hydroxystyrene-co-tertbutyl acrylate) resin, onium salt photoacid generator, and an inert plasticizer. Deprotection rates were measured as a function of catalyst loading, plasticizer loading, and temperature (always below the polymerâĂŹs glass transition). Experimental data were interpreted with a simple and efficient model based on anomalous acid diffusion and a phenomenological second-order acid loss. This model predicted key aspects of the macroscopic deprotection rates, such as fast reaction at short times, slow reaction at long times, and a nonlinear dependence on acid loading. Reducing the size of the acid-counterion pair, adding an inert plasticizer, or increasing the temperature will enhance acid transport rates and reduce the anomalous character. These behaviors suggest that acid diffusion is coupled to dynamical properties of the glassy polymer resin.

To complement analysis of bulk kinetics, we simulated nanopattern formation

using the anomalous acid transport model, and then compared predictions with experimental line widths. The simulations include a spatial distribution of acid catalyst that reflects the exposure statistics in electron beam lithography experiments. However, while experiments include a pattern development step that dissolves the reacted polymer, the simulations do not yet have this module. Nevertheless, the predicted and measured pattern dimensions are in qualitative agreement, suggesting that lithographic resolution in CARs might be predicted from simple spectroscopy measurements coupled to spatially-resolved simulations.

# Table of Contents

Acknow	wledge	ements	iv
Abstra	nct		vi
Table o	of Con	${f vients}$	iii
List of	Figur	es	xi
List of	Table	95	vi
Chapte	e <b>r 1</b> ]	Introduction	1
1.1	Projec	ction lithography overview (Top down approach)	2
1.2	Patter	rn resolution	4
Chapte	er 2	Chemically amplified resists	<b>5</b>
2.1	DUV	resists (248 to 193 nm)	6
2.2	Chem	ical amplification	7
2.3	Furth	er developments: ESCAP resists	9
2.4	193 ni	m resists	10
2.5	Extre	me UV resists	11
Chapte	er 3 ]	Diffusion in gases and liquids	.2
3.1	Diffus	sion in solids	13
3.2	Diffus	sion in polymers	14
	3.2.1	Glass transition	14
	3.2.2	Free volume theory	15
	3.2.3	Spatially heterogeneous dynamics	19

3.3	Previo	ous acid diffusion experiments	22
	3.3.1	Single layer experiments	23
	3.3.2	Bilayer experiments	24
	3.3.3	Trilayer experiments	27
Chapte	er 4	Model chemically amplified resist	29
	4.0.4	Resin	29
	4.0.5	Photoacid generators (PAGs)	30
	4.0.6	Plasticizer	30
	4.0.7	Base quencher	31
	4.0.8	Solvent	31
4.1	Depro	otection reaction	31
	4.1.1	Previous studies of this system	34
Chapte	er 5	Bulk deprotection experiments	38
5.1	Introd	luction	38
5.2	Exper	rimental Procedures	40
	5.2.1	Materials	40
	5.2.2	Extinction Coefficient	41
	5.2.3	Acid Generation	41
	5.2.4	Sample Preparation	42
	5.2.5	Fourier Transform Infrared Spectroscopy (FTIR) $\ldots$	44
	5.2.6	Glass Transition Temperature	46
5.3	Simul	ation Methods	46
5.4	$\operatorname{Resul}^{2}$	ts	48
5.5	Concl	usions	57
Chapte	er 6	Characterizing acid diffusion lengths	59

6.1	Procee	dures
	6.1.1	Materials
	6.1.2	Deprotection experiments
	6.1.3	Analysis of deprotection experiments
	6.1.4	Nanopatterning
	6.1.5	Simulations of nanopattern formation
6.2	Result	s and discussion
6.3	Conclu	usions
Chapt	er 7 (	Dutlook
	7.0.1	Objective of trilayer experiments
	7.0.2	Construction of trilayer
Refere	nces .	
Chapt	er A	Appendix

# List of Figures

Figure 1.1	Schematic of lithography process showing positive and nega-	
	tive routes.	3
Figure 2.1	Schematic illustration of (a) DNQ/novolac resist solubility	
	switch (b) chemical amplification.	8
Figure 3.1	Schematic illustration of 3 major mechanisms of diffusion in	
	solids: (a) vacancy (b) interstitial and (c) interstitialcy. $\ $ .	14
Figure 3.2	Illustration of division of specific volume of an amorphous	
	polymer (Kumar 1997 [1])	16
Figure 3.3	Illustration of a typical two stage sorption isotherm. Relative	
	mass uptake of 1 is also known as Fickian saturation level.	
	(Van der Wel, 2000 [2]) $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$	19
Figure 3.4	Illustration of spatial heterogeneities near $T_g$ . Diameter of the	
	region is on the order of $\xi_{het}$ and evolves with time t. (adapted	
	from Ediger 2000 [3]) $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	21
Figure 3.5	Bilayer sample, with feeder layer on top, showing acid activa-	
	tion and post-exposure steps.	25
Figure 3.6	Trilayer sample, with feeder layer on top, showing acid acti-	
	vation and post-exposure steps.	28
Figure 4.1	Structures of (a) $P(HOST-co-tBA)$ and (b) $P(S-co-tBA)$ resins.	
	29	
Figure 4.2	Chemical structures of photoacid generators (a) PFBS and	
	(b) Tf	30

Figure 4.3	Acid-counterion pair $(H^+A^-)$ generation from PFBS after ex-	
	posure to UV	32
Figure 4.4	Overall deprotection reaction where $H^+A^-$ denotes acid-counteries	on
	pair	33
Figure 4.5	Simulation approach used by Hinsbeg and co-workers to model	
	acid tranport. Resist is represented as a stack of homogenous	
	slabs with diffusion occuring between the layers described	
	Fickian kinetics.	35
Figure 4.6	Two types of systems used by Kang and co-workers	36
Figure 5.1	Determining acid generation efficiency with Dill's method.	
	Contrast curves for PFBS (a) and Tf (b). Best-fit lines to	
	calculate Dill C parameter for PFBS (c) and Tf (d) in units	
	of $\mathrm{cm}^2/\mathrm{mJ}.$ The dashed curves in (a) and (b) are drawn to	
	guide the eyes and are not fits to the data. $\ldots$ $\ldots$ $\ldots$	43
Figure 5.2	IR absorbance data for $\mathrm{P}(\mathrm{HOST\text{-}co\text{-}tBA})$ resist with 1 wt%	
	Tf and 10 wt% DOP, deprotected at 80°C. The peak at 1149	
	$\rm cm^{-1}$ is associated with C-O-C stretches of tBA moieties.	45
Figure 5.3	(a) Overall deprotection reaction with a cid-counterion $\rm H^+X^$	
	(b) PFBS counterion. (c) Tf counterion. (d) Plasticizer (DOP).	48
Figure 5.4	$\mathrm{T}_g$ measurement P(HOST-co-tBA) film with 1 wt% PFBS and	
	10 wt% DOP. (Cooling cycle.) $\ldots \ldots \ldots \ldots \ldots \ldots$	49
Figure 5.5	Master curve for Tf with 10 wt% DOP and reaction temper-	
	ature of 90°C. Solid line reports the best-fit to a first-order	
	reaction (Equation 5.6).	50
Figure 5.6	Apparent order $n$ as a function of temperature for each resist	
	formula.	51

Figure 5.7	Measured deprotection rates with best-fit to the anomalous			
	diffusion model. Open/closed symbols designate resists with/with the transformation of transformation of transformation of the transformation of transfor	hout		
	DOP. (a) Tf counterion at 70°C; (b) PFBS counterion at 70°C.			
	Inset plot reports the residuals.	53		
Figure 5.8	Times required for $50\%$ deprotection as a function of temper-			
	ature and acid loading. Experiments are compared with the			
	optimized simulations for each formula: (a) Tf, (b) Tf + DOP,			
	(c) PFBS, (d) PFBS + DOP. $\ldots \ldots \ldots \ldots \ldots \ldots$	54		
Figure 5.9	(a) Characteristic diffusion rate $1/ au$ as a function of tempera-			
	ture. (b) Anomalous exponent $\gamma$ as a function of temperature.			
	Note that $\gamma < 1$ reproduces subdiffusive transport, while $\gamma =$			
	1 represents Fickian transport	55		
Figure 6.1	Simulation algorithm illustrated in two-dimensions for clarity.	62		
Figure 6.2	Initial spatial distribution of PFBS catalyst for nanopattern-			
	ing simulations.	66		
Figure 6.3	Experimental deprotection levels (symbols) and best-fit sim-			
	ulations (lines) for 1 wt%, 2 wt%, and 4 wt% acid loading. a)			
	70 °C, b) 80 °C, c) 90 °C, and d) 90 °C with 10 wt% DOP	67		
Figure 6.4	a) Deprotection rate $1/\tau$ as a function of temperature; b)			
	Anomalous exponent $\gamma$ as a function of temperature. Note			
	that $\gamma < 1$ reproduces subdiffusive transport, while $\gamma = 1$			
	represents Fickian transport.	69		

Figure 6.5	a) Line width for each resist formula as a function of exposure			
	dose. b) Examples of SEM measurements for each formula, ex-			
	posure dose of 600 $\mu { m C/cm^2}$ . c) Normalized residual thickness			
	(NRT) for each resist formula as a function of deprotection			
	level (30 sec development)	71		
Figure 6.6	a) Image maps of simulated deprotection level (averaged through			
	film thickness) for 30 sec PEB at 90°C. b) Deprotected line			
	width at 30 sec and initial spatial density of acid catalyst. $% \left( {{\left( {{{\left( {{{\left( {{{\left( {{{\left( {{{\left( {{{c}}}} \right)}} \right.}$	73		
Figure 7.1	A sample trilayer geometry. Top (feeder) layer is loaded with			
	photoacid generator.	76		
Figure 7.2	Optical microscopy images of spin-coated PHOST layer on			
	PMOS+PAG layer. (a) shows a conformal bilayer with 1-			
	butanol as solvent for PHOST (b) shows a non-conformal film			
	when anhydrous ethanol was used as a solvent for PHOST.	78		
Figure 7.3	Optical microscopy image of a PtBA film stamped on top of a			
	PMOS layer using PDMS samping method. (a) shows a hole			
	left behind due to uneven release of the film from PDMS slab			
	(b) zoomed in version of (a) shows wavy nature of the film.	79		
Figure 7.4	Optical microscopy image of a 2 in $\times 2$ in trilayer. (a) Area			
	of the trilayer shows some cracking of the detector layer. (b)			
	Area from the same trilayer that is uniform. A 250 $\mu {\rm m}$ circle			
	in the middle shows approx. area of the IR beam. $\ldots$ .	80		
Figure 7.5	FTIR heat cell for trilayer experiments.	81		

Figure 7.6	igure 7.6 A trilayer diffusion experiment showing reduction in IR al				
	sorbance of tBA group at 1150 $\rm cm^{-1}$ implying diffusion of				
	acid catalyst across 4 nm PHOST film into the detector layer.				
	Heat cell was not used for this experiment.	82			
Figure 7.7	$In\ situ$ trilayer diffusion experiment showing IR absorbance				
	vs. time. The drop in absorbance is indicative of onset of acid				
	in detector layer. $t_{\rm diff}$ is time required for diffusion through				
	intermediate layer [4]	83			
Figure A.1	Correlation plot for $\tau$ vs. $\gamma$ in each formula	102			

# List of Tables

Table 3.1	Examples of relaxation time scales $( au)$ at temperatures near		
	$T_g$ and effect of experimental temperature on the time scale $\left[58\right]$	20	
Table 4.1	Diffusion coefficients and activation energies	35	
Table 4.2	Arrhenius parameters for reaction and diffusion constants [9].	37	
Table 5.1	Contents of a formula	43	
10010 0.1		10	
Table 5.2	Key IR peak assignments for $P(HOST-co-tBA)$	44	
Table 5.3	$T_g$ values of P(HOST-co-tBA) formulas	49	
Table 5.4	Activation energies for acid diffusion $(E_a)$	56	
Table 7.1	Working trilayer scheme	80	
Table A.1	Time (sec) required for $50\%$ deprotection. Sim = Simulation,		
	Ex = Experiment.	102	

## Chapter 1 Introduction

Lithography is the backbone of modern Integrated Circuit (IC) manufacturing. There are various processes in constructing integrated circuits, and historically it has been the lithographic step that limits the smallest feature that can be printed. The term lithography comes from Greek words "Lithos" (stone) and "Graphein" (to write) and was a technique used to print maps or artwork on limestone in the 18th century. The image to be printed was drawn with oil or grease into the limestone, and then the stone was treated with a mixture of acid or gum (etchant) which would etch away all the area that are not protected by oil or grease. In a subsequent step, the stone was immersed in water and water would be retained by the etched area and be repelled by the areas under oil or grease (image). When an oil based paint was applied to this stone, the color would only stick to the original image and be repelled by water creating the final (relief) image. Lithography, after its invention by Alois Senefelder in 1796, was mostly used to publish theatrical works [10]. With technological advances, it became the most popular form of printing in the United States in early 19th century. Another important invention in lithography came in 1826 when French scientist Niepce invented photography, where light was used to create the image for the first time instead of hard plates that were used as stamps [11]. It would be another century before photography evolved into photolithography which would be used to fabricate ICs.

The term photolithography (or optical lithography) is used to describe the modern microfabrication technology that is used to create integrated circuits and microelectromechanical systems with submicron size features. A desired image (such as a circuit) is shined on a thin radiation-sensitive film and then it is transferred to the substrate beneath using various chemical and physical processes. This approach is also known as "top down" approach and is used for virtually all commercial microfabrication. Alternatives to photolithography, such as "bottom up" approaches, are still in the research phase.

## 1.1 Projection lithography overview (Top down approach)

Advances in projection lithography have enabled better device performance while reducing costs, a trend seen in the semiconductor industry for past several decades. Intel's first microprocessor had only 2300 transistors per chip at half-node (half the distance between adjacent memory cells) of 10  $\mu$ m in 1971. Since then the number of transistors per chip has doubled roughly every 18 months while feature size has shrunk down, a prediction first made by Intel co-founder Gordon Moore in 1965, hence known as Moore's law. Intel produced transistors with 1  $\mu$ m critical dimension (CD; smallest feature size) with a little over million transistors per chip in 1989. In 2014, at 22 nm CD, Intel's 'Ivy Bridge' microprocessor has 4.3 billion transistors. This miniaturization has been largely enabled by improvements in lithographic tools, methods, and materials [12].

Projection lithography projects light through a photomask and multiple lenses (optics). The pattern of exposed areas represents the required circuit geometry. Irradiation is the first step in a chemical reaction (chain scission, crosslinking, or deprotection) that changes the polymer's polarity. The more soluble regions of the film can then be washed away with an appropriate solvent, generating a relief image (topographical). Figure 1.1 describes an oversimplified schematic of the lithographic process.

A resist film is applied on a silicon wafer using spin coating. A short bake step, usually known as prebake, helps to drive out the residual solvent from the resist.



Figure 1.1: Schematic of lithography process showing positive and negative routes.

The photoresist is then exposed to light through a photomask. In the following postexposure bake step, the exposed areas undergo reactions that alter their chemistry depending on the contents and type of the resist. This switch in chemistry changes its solubility in a special solution called developer, and depending on the 'tone' of the resist, the exposed regions either wash away (positive tone resist) or stay on the Si substrate (negative tone resist). Once the patterns have been developed, the pattern is transferred to the wafer by etching and deposition processes. After the pattern transfer step, the photoresist is no longer needed and has to be removed. A popular way of doing this is to use a 'resist stripper' that dissolves the photoresist.

### **1.2** Pattern resolution

The minimum feature size that can be printed sets the resolution and is one of the most important driving factor of innovations in lithography. Resolution in lithography is similar to resolution in optical microscopy. The smallest feature than can be resolved is proportional to the wavelength of imaging light, and inversely proportional to the numerical aperture of the lens system. The smallest feature size that can be printed with projection lithography is given by the Rayleigh equation,

$$CD = k_1 \frac{\lambda}{NA}.$$
(1.1)

CD (Critical Dimension) is the feature size,  $\lambda$  is the exposure wavelength, NA is numerical aperture of the lens, and  $k_1$  is a process dependent factor, usually between 0.25-0.70 [13].

Wavelength of the light source has been a major factor in increasing resolution in ICs. Until late 1980s, mercury (Hg) discharge lamps were used for exposure to get 436 nm (g-line) and 365 nm (i-line) wavelength. The lithography process resolutions were 400 nm and 350 nm, respectively. Transitioning to shorter wavelengths, the first generation of krypton fluoride (KrF) excimer lasers provided a wavelength of 248 nm increasing the resolution to 150 nm. Argon fluoride (ArF) excimer lasers provided exposure of  $\lambda$ =193 nm and further increased the resolution to 80 nm [14]. Several resolution enhancement techniques (RETs), such as multiple patterning and immersion lithography, have since helped increase the resolution to what it is today, 14 nm CD [15] while keeping wavelength of the source at 193 nm.

## Chapter 2 Chemically amplified resists

Before described the development and function of chemically amplified resist, it is important to highlight and define the factors that make a resist a good candidate for lithography.

- Sensitivity: Sensitivity denotes the amount of incident energy required to carry out photochemical events in the resist. Higher sensitivity means lower amount of radiation energy required and hence higher photospeed.
- **Resolution:** The smallest feature size that can be reproduced from the photomask/aerial image.
- **Contrast:** Resist contrast is the ability of the resist to distinguish between light and dark regions of the photomask. High contrast resist provides resolution.

Apart from these important criteria, a "good" resist also provides high dry-etch resistance, high thermal stability, wide process latitude, and good adhesion with underlying substrate, among many other factors.

The main driving factor behind achieving higher resolution has been a reduction in the wavelength of the exposure source. As the wavelength goes down, the material and exposure tools have to be tailored accordingly to get the optimum performance. One of the first resist system used for production in 1970s was diazonaphthoquinone (DNQ)/novolac. It was the workhorse of ultraviolet (UV, 436 to 365 nm) wavelengths [15]. DNQ, a photoactive compound, acts as a dissolution inhibitor for the novolac resin in an aqueous base developer. When DNQ/novolac film is exposed to UV, DNQ undergoes a series of reactions to form a base soluble compound that enhances the dissolution of novolac in the aqueous base developer. With some modifications in absorption characteristics of DNQ, DNQ/novolac was also used for mid-UV (300-350 nm) light sources [16]. Further migration towards deep UV (DUV, 254 nm) sources needed development of new resist materials and chemistry mainly because, the absorption coefficient of DNQ/novolac resist was too high at DUV wavelengths. As a result of poor transparency, these resists had low sensitivity, and the relief images had sloping side walls [17].

### 2.1 DUV resists (248 to 193 nm)

In early 1980s, researchers at IBM successfully demonstrated krypton fluoride (KrF) excimer lasers as an exposure source (operating at 248 nm) and proposed it as an alternative for then state-of-the-art mercury arc lamp sources [18]. A few years later in 1990, use of argon fluoride (ArF) excimer lasers drove further reductions in wavelengths down to 193 nm, which is used for semiconductor manufacturing to this day. Use of excimer lasers instead of Hg lamp provided higher resolution and at least 2 orders of magnitude faster throughput [19]. The real challenge was to develop new materials that will overcome performance limitations posed by the existing DNQ/novolac system.

Poly(methylmethacrylate)(PMMA) was one such alternative that had been studied since late 1970s. It provided higher DUV absorption and better resolution and was seen as a promising candidate [20]. The major drawbacks PMMA suffered from were poor sensitivity and low dry-etch resistance, precluding its use as DUV resist in manufacturing. A negative tone resist comprised of a photoactive azide compound and polyhydroxystyrene (PHOST) as base-soluble matrix was the first successful DUV resist [21]. However, it was highly opaque and resulted in undercut profiles. Another alternative approach was to modify existing DNQ/novolac system and extend its usability. One such effort [17] involved incorporating a chromophore into the existing dissolution inhibitor (photoactive compound) to boost absorption in DUV region. However, the sensitivity improvement was too marginal and since aliphatic polymers (such as PMMA) break down easily, they suffer from low etch resistance.

In general, 193 nm DUV resists could be formulated with the desired optical transparency, but low sensitivity and poor etch resistance precluded their use in semiconductor manufacturing. Sensitivity improvement was the focus of much research since as the wavelength of the source was reduced, more optical elements were introduced in the path of the beam which limits the intensity of the light at the point of exposure. Imaging mechanisms based on absorption of multiple photons for each photochemical event showed inherently limited sensitivity [15].

## 2.2 Chemical amplification

In 1982, IBM researchers Willson, Ito, and Frechet published their work on "New UV resists with negative or positive tone" [22] wherein they introduced the concept of "Chemical Amplification" for orders of magnitude improvement in sensitivity. These materials are comprised of a polymer resist and photosensitive catalyst that drives reactions in the polymer. Quantum yield, expressed as number of molecules transformed per photon absorbed, is used to characterize efficiency of the photochemical events. Typical DNQ/novolac resist had a quantum yield of 0.2-0.3, meaning to convert one molecule of photoactive compound 3-5 photons were needed. Considering the low energy available at the resist surface, bringing the quantum yield to its theoretical limit of 1 wasn't going to be of much help for DUV, X-ray, and electron beam lithography. In chemically amplified (CA) resists, the photogenerated catalyst generated can drive hundreds of chemical transformations hence "amplifying" the effect of photon (s) needed to generate the catalyst. This gain mechanism (Figure 2.1) offered an unprecedented improvement in sensitivity, so CA resists started to attract significant



Figure 2.1: Schematic illustration of (a) DNQ/novolac resist solubility switch (b) chemical amplification.

attention for high throughout semiconductor manufacturing. Three major types of imaging schemes were developed based on the concept of chemical amplification: [23]

- Cross linking of epoxy resins to provide negative tone resist;
- Deprotection (cleavage) of pendant groups to provide negative or positive tone resist, depending on the type of developer selected;
- Depolymerization followed by evaporation of monomers in polyaldehydes, providing a self-developing positive tone resist.

Out of these, deprotection route was pursued by the team at IBM. The idea was to create a nonpolar polymer with acid-labile pendant protecting groups, and convert it in to a polar one through chemically amplified (acid catalyzed) deprotection. An early example of this chemistry is poly(4-hydroxy- $\alpha$ -methoxystyrene) [24]. The photoactive compound in the resist formula was an onium salt cationic photoacid generator. Resist could be used both in negative or positive mode depending on whether organic or aqueous developer was used. Negative tBOC resist process gained widespread acceptance in lithography community after its high resolution capabilities were demonstrated, [25] leading to its use for the first time in production of 1Mb DRAMs (Dynamic Random Access Memory) in DUV mode at IBM [26]. Chemically amplified resists were now being seen as viable alternative for DNQ/novolac resists.

### 2.3 Further developments: ESCAP resists

Chemical amplification gained acceptance among lithographers because of high resolution, high sensitivity due to acid catalyst, and design flexibility that could be achieved due to negative or positive tone imaging depending on the choice of developer [27]. However, lipophilic films such as tBOC resist in negative mode suffered from drawbacks like poor adhesion to the substrate and failure to develop cleanly [27]. The more challenging problem that prevented tBOC resist from being used in positive tone was skin or T-top formation (an insoluble surface layer) during the post exposure delay (PED), the time between coating the film and post exposure bake, especially after exposure. A particular organic base, N-methylpyrolidone (NMP), was identified by researchers as the issue. Even trace amounts (of the order of 15 ppb) of this basic substance present in the environment can adsorb on to the surface and interfere with catalytic activity of the acid by neutralizing it [28]. Researchers addressed this issue with various approaches [15] like purifying the air inside the enclosing atmosphere, applying a protective overcoat that will hinder basic contaminants from reacting with acid catalyst, and including additives in resist formulation. More fundamental approaches included reduction of the activation energy required for deprotection, hence eliminating the need for post-exposure bake, or reduction in the free volume by annealing in order to reduce the uptake of NMP [15].

One way to achieve better annealing (and hence free volume reduction) was to employ a low  $T_g$  resist. This had been validated by studying NMP uptake in low and high  $T_g$  isomers of tBOC resist [29]. However, low Tg resists were ruled out because they couldn't be used for high temperature fabrication. The other option was to design a resist (base polymer and PAG) that has high Tg and can withstand high temperatures to achieve better annealing.

An Environmentally Stable Chemically Amplified Positive tone (ESCAP) resist introduced in 1994 by researchers at IBM sought to do just that and much more [30]. 4-hydroxystyrene (HOST) and t-butyl acrylate were used as monomers to build a copolymer poly(HOST-co-tBA) ( $T_g \sim 150^{\circ}$ C). Base soluble PHOST would become lipophilic when copolymerized with t-butyl acrylate (tBA). Deprotection would convert some fraction of the tBA groups to acrylic acid (AA), which is soluble in an aqueous developer soluble in an aqueous developer. The details of the reaction will be discussed in depth in following sections. PAG used, in the initial report, was N-camphorsulfonyloxynaphthalimide. The developer used for positive imaging was aqueous base, typically 0.21 N tetramethylammonium hydroxide (TMAH). Resist showed extremely low uptake of base contaminant at high post apply bake temperature (150°C), which is why this is termed environmentally stable. Apart from being environmentally and thermally stable, ESCAP resist showed 0.25  $\mu m$  resolution on 248 nm KrF excimer laser stepper in a dose range of 30-40  $\mu C/cm^2$  [30]. ESCAP resist showed an extra ordinary resolution of 200 nm with 0.53 NA (numerical aperture) tool operating in DUV (248 nm) and hence was selected for commercialization of 256 MB DRAM production.

#### 2.4 193 nm resists

After 248 nm, lithographers started working on resist materials for 193 nm. PHOST based resists operating on deprotection mechanism were popular for 248 nm mode. However, PHOST suffers from excessive absorption at 193 nm. Excessive absorption would mean radiation not being able to reach the bottom of the film, leaving it unexposed. Poly(methylmethacrylate), which was earlier discarded due to low  $O_2$  etch resistance, was proven to show higher etch resistance after incorporation of bi- or tri-alicyclic pendant groups such as norbornene or adamantane along the polymer backbone [31, 32]. Chemical amplification, however, remained the central theme of imaging mechanism by inclusion of acid-labile ester functionality along the backbone. Polymethacrylate based resists and many copolymers of different types of monomers have become the workhorse of the 193 nm lithography.

### 2.5 Extreme UV resists

157 nm ( $F_2$  excimer laser) lithography was abandoned by semiconductor industry for various reasons. The chip resolution, however, continued to increase owing to techniques like double exposure or multiple patterning. After 193 nm, a potential lower wavelength candidate is extreme UV (EUV) light source ( $\lambda = 14$  nm). However, EUV exposure tools suffer from low brightness. Therefore, apart from higher resolution requirement (<25nm), EUV technology also demands resists that show high sensitivity (<10 mJ/cm<sup>2</sup>). This is one of the reasons why CA resists (copolymers of PHOST with other monomers) are likely to be used as EUV resists. EUV resists are also expected to show low (<2 nm) line edge roughness in the relief image [33]. High resolution, high sensitivity, and low LER are difficult to achieve simultaneously and a trade off exists between the three. For example, resolution and low LER has also been achieved by molecular glass, where photoacid cation is covalently bound to the backbone hence reducing photoacid diffusion. Molecular glass resists offer high resolution and low LER, but the sensitivity is poor [34].

## Chapter 3 Diffusion in gases and liquids

Diffusion of solutes in gases, liquids, and certain types of solids is well-understood through theory and experiment. Diffusion in gases and liquids depends on solute size, temperature, pressure, and viscosity of the medium. Diffusion in solids can be slower by many orders of magnitude as compared to fluids. The objective of this chapter is to review classical diffusion theory for simple materials systems, and introduce the challenges for modeling diffusion in inert and reactive polymers.

Classical diffusion theory is based on Brownian motion. Brownian motion is the motion of the particle suspended in a fluid resulting from its collision with atoms or molecules in its surrounding. Diffusion is defined as the mass transfer of a material from a region of high concentration to low concentration resulting from such random movements. It was formalized by Fick in 1855. Fick's first law is

$$J = -D\frac{dC}{dx},\tag{3.1}$$

where J is the rate of net transfer of material from a unit area in a small amount of time, C is the concentration of the substance, x is the distance in the direction perpendicular to the plane of diffusion, D is the constant of proportionality known as diffusion coefficient for that system. Fick's second law predicts how concentration changes with time and can be calculated using following partial differential equation

$$\frac{\delta C}{\delta t} = D\left(\frac{\delta^2 C}{\delta x^2} + \frac{\delta^2 C}{\delta y^2} + \frac{\delta^2 C}{\delta z^2}\right),\tag{3.2}$$

where t is time. Diffusivity D is constant with respect to time and position in this formalism.

Fick's laws have been used to study transport phenomena in various systems and applications such as biomembranes [35], pharmaceutical research [36], foods [37], human population dynamics [38], nuclear materials [39] and semiconductor doping process [40], and these models have proved very useful.

### 3.1 Diffusion in solids

There are three major mechanisms by which an atom diffuses in a solid: vacancy mechanism, interstitial mechanism, and intersticialcy mechanism. Vacancy diffusion occurs when atoms exchange with vacancies that are already present or have been deliberately created to facilitate diffusion. This mechanism is also known as hole hopping and is illustrated schematically in Figure 3.1(a). The diffusion rate depends on the number of vacancies and the activation energy required for hopping. The direction of flow of atoms is opposite of the direction of flow of holes. Interstitial diffusion refers to diffusion of species through the interstitial void as illustrated in Figure 3.1(b). Interstitial diffusion is generally faster than vacancy diffusion due to the fact that most interstitial voids are vacant because of lower solubility of interstitial atoms such as C, H or O. Interstitial diffusion is also faster in polycrystalline materials, as opposed to single crystal materials, owing to faster diffusion along grain boundaries. When the interstitial atom becomes too large and may cause distortion of lattice network, they start moving by interstitialcy mechanism. The diffusing atom pushes a lattice atom into interstitial void and occupies the now vacant lattice site itself as illustrated in Figure 3.1(c).

Diffusion in solids is highly dependent on temperature, activation energy, type of mechanism, and crystalline nature. The temperature dependence is given by an Arrhenius type expression



Figure 3.1: Schematic illustration of 3 major mechanisms of diffusion in solids: (a) vacancy (b) interstitial and (c) interstitialcy.

$$D = D_o \exp\left(\frac{-Q_d}{RT}\right). \tag{3.3}$$

 $D_o$  is a temperature-independent preexponential,  $Q_d$  is activation energy of diffusion, R is ideal gas constant, and T is absolute temperature. Surface hardening of metals and doping in semiconductors are practical examples of diffusion in solids.

### **3.2** Diffusion in polymers

Polymers are an interesting case between fluids and solids, and hence they are much more complex to understand and attract a lot of attention. Behavior of the polymers is highly dependent on temperature. Polymers at high temperature in are in a melt state and at low temperature are in a glassy solid state. The temperature that describes the transition between melt and glassy state is known as glass transition temperature.

#### 3.2.1 Glass transition

When a stable liquid is cooled at constant pressure, it solidifies at its melting temperature. A liquid that does not solidify at melting temperature is called a supercooled liquid. Amorphous polymers act as supercooled liquid when cooled below the glass transition. As the temperature is lowered through the glass transition, the density and viscosity increase, and polymer motions and rearrangements become so slow that equilibrium volume cannot be reached. Therefore, the experimentally observed specific volume is higher than the theoretically expected specific volume. The polymer is frozen in a state known as a glass. This process of glass transition does not occur suddenly at a single temperature, but occurs over a small range of temperature. The midpoint of this temperature range is known as glass transition temperature ( $T_g$ ). Differential scanning calorimetry is a widely used technique to calculate the  $T_g$  value [41]. It detects the change in heat capacities between melt and glass state. The range of glass transition and value of  $T_g$  very much depends on the rate of cooling and heating cycle. Spectroscopic ellipsometry can also be used to measure  $T_g$  where it detects changes in thermal expansion as the film is heated through the glass transition.

#### 3.2.2 Free volume theory

A widely used method for describing penetrant diffusion in a polymer (both in melt and glassy states) is the application of free volume theory. It is based on theoretical framework proposed by Cohen and Turnbull [42]. The free volume theory suggests that specific volume of a polymer and penetrant mixture is based on three components. The occupied volume is the volume of the system at 0 K. The remaining volume, known as free volume, is made up of two components: Interstitial free volume and void free volume as shown in Figure 3.2. Interstitial free volume is uniformly distributed among molecules of the system, and energy required for its redistribution is large. The void free volume is redistributed without an increase in energy and hence taken as the free volume that is available for diffusional transport. The size and location of these pockets of diffusional free volume depends on thermal history, mobility of the polymer side chain groups, and polymer chain flexibility [43]. It is



Figure 3.2: Illustration of division of specific volume of an amorphous polymer (Kumar 1997 [1])

clear from this theory that two requirements must be met for diffusion to occur:: a void of sufficient size must appear in the vicinity of the penetrant, and penetrant must acquire enough energy to jump into the void. The diffusion coefficient, without loss of generality, is expressed by following form [44]

$$D = D_o \exp\left[\frac{-\gamma V_1^*}{V_{FH}}\right] \exp\left[\frac{-E^*}{kT}\right].$$
(3.4)

 $D_o$  represents a constant preexponential factor.  $\gamma$  is the overlap factor since same free volume is available for more than one penetrant. Its value is between 0.5 to 1.  $V_1^*$  is the critical hole free volume (minimum volume required for jump to occur) and  $V_{FH}$  is the average hole free volume per unit mass of the mixture.  $E^*$  represents the effective energy per mole required by the penetrant to overcome attractive forces exerted by its neighbors. It should be noted that the diffusion process will be limited by the least probable mechanism (probability of void appearing vs. acquiring sufficient energy for jump). As a special case of Equation (3.4), in a dense system, specific hole free volume available will be lower, especially at temperatures closer to glass transition, and hence diffusion will be controlled by free volume effects rather than probability of acquiring necessary energy [45]. Hence, the energy term from Equation (3.4) can be absorbed in to preexponential factor leading to a simplified version

$$D = D_o^* exp\left[\frac{-\gamma V_1^*}{V_{FH}}\right]. \tag{3.5}$$

The hole free volume  $(V_{FH})$  is given by

$$V_{FH} = V_0 \alpha_f (T - T_0), \tag{3.6}$$

where  $\alpha_f$  is the thermal expansion coefficient of free volume in melt state,  $T_0$  is the temperature at which free volume will vanish and  $V_0$  is the volume at  $T_0$ . Equations (3.5) and (3.6) combined give the empirical equation that incorporates the non-Arrhenius character as the temperature is lowered, which is known as Vogel-Tamman-Fulcher (VTF) equation [46].

#### Diffusion in glassy polymers

As temperature is reduced below the glass transition temperature  $(T_G)$ , excess free volume is generated as illustrated in Figure. 3.2, Hutchinson and Kivas [47] extended free volume theory to non-equilibrium glassy state by introducing excess free volume  $V_{EX}$ :

$$V_{EX} = V_0 - V_{EQ}, (3.7)$$

where  $V_0$  is the total free-volume and  $V_{EQ}$  is the equilibrium free-volume. This is known as excess free volume (EFV) theory [48]. EFV theory assumes free volume distribution to be mechanism of transport even in glassy state below  $T_g$ . It looks at the transport of penetrant in glassy state as motion of mobile penetrant in a glass made up of immobile molecules, and has been regarded as oversimplified since it does not take in to account the energy term for penetrant migration [49].

Vrentas et al [43] also proposed a modification of Equation (3.4) to extend it in to glassy region. In the limit of zero penetrant concentration in polymer glass, it can shown that

$$V_{FH} = V^0(T_g) \left[ f_H^g + (\alpha_{2g} - \alpha_{c2g})(T - T_g) \right], \qquad (3.8)$$

where  $V^0(T_g)$  is the specific volume of the polymer at its glass transition temperature  $(T_g)$ ,  $f_H^g$  is the fractional hole free volume of the polymer at  $T_g$ , T is any temperature below  $T_g$ ,  $\alpha_{2g}$  is the thermal expansion coefficient of the polymer, and  $\alpha_{c2g}$  is the thermal expansion coefficient of the specific occupied volume and specific interstitial free volume for the glassy polymer. Wang *et al* have studied diffusion of toluene in glassy polystyrene and used Equation (3.8) to calculate free volume. The data-theory comparison shows an average absolute error of 10%. Another data-theory comparison was done by Ramesh and Duda [50]. They studied diffusion of trace amounts of styrene in glassy polystyrene. They found good agreement between data and theory for three out of four temperatures used for studies. These two studies indicate that free volume theory can give reasonably good predictions for polymer-penetrant diffusion within classical Fickian framework.

#### Non-Fickian anomalies

Free volume theory, although shown applicable in some cases, falls short to explain outcomes of vapor sorption studies [51-54]. Vapor sorption studies are carried out to find out equilibrium uptake of various solvents (usually water). A sorption isotherm is a plot of relative mass uptake of penetrant (kg/kg) vs. square-root of time  $(s^{1/2})$ . In case of Fickian diffusion, one will expect a linearly increasing uptake with square root of time. The vapor sorption analysis by the aforementioned studies were done assuming Fickian diffusion process, but a two stage sorption isotherm was observed in all cases. A two stage isotherm is made of a initial Fickian type behavior and then a deviation from linearity at longer times as can be seen Figure 3.3.



Figure 3.3: Illustration of a typical two stage sorption isotherm. Relative mass uptake of 1 is also known as Fickian saturation level. (Van der Wel, 2000 [2])

#### 3.2.3 Spatially heterogeneous dynamics

Free volume theory's implication that density reduction is responsible for sluggish polymer movement near and below  $T_g$  has been refuted for not being "fundamentally sound" enough and some experiments have shown that this can be rejected for some fragile glass formers [3]. Some experiments backed by simulation studies paint a completely different microscopic picture of what might be happening when a polymer is cooled towards its glass transition temperature [55]. As the temperature goes down in polymers, the timescale of the molecular rotation dramatically increases. Table 3.1 shows some relaxation time scale increment in polymers or ionic liquids as glass transition temperature is approached from above. Molecular rotation time and relaxation Table 3.1: Examples of relaxation time scales ( $\tau$ ) at temperatures near  $T_g$  and effect

of experimental temperature on the time scale [5–8]

Sample	$T_g$ (K)	T(K)	T- $T_g$ (K)	$ au~({ m ms})$
Poly(ethyl methacrylate)	345	335	-10	10
Doly(mothyl motherylate)	308	413	15	0.15
r ory(methyr methacrylate)	290	407	9	3
Deluigennene	206	229	23	0.5
Poryisoprene	200	210	4	10
Lithium chlorido H O	144	173	29	0.00025
Litinum chloride-1120	144	151	7	6.6

times associated with viscosity are collectively known as  $\alpha$ -relaxation process. As the temperature is lowered, due to lower thermal energy available, molecules in a polymer start moving as a group in a cooperative motion. These groups are known as cooperatively rearranging regions (CRR) since they are constantly changing their shapes and size as shown in Figure 3.4. Tracht *et al* found the CRR size to be ~3 nm for polyvinylacetate at 10 K above  $T_g$  [56]. The relaxation time of each domain may vary dramatically from its neighbors. Collectively, these relaxation functions can be fit to Kohlrausch-Williams-Watts (KWW) stretched exponential function,

$$CF(t) \approx exp[-(t/\tau)^{\beta}]),$$

where  $\tau$  is the characteristic relaxation time, and  $\beta$  represents deviation from the exponential behavior. At high temperatures,  $\beta$  is closer to 1 and decreases to about 0.5 near  $T_g$  [3]. This non-exponential relaxation allows us to look at the system in two different ways. One scenario where the local dynamics are heterogeneous and each domain relaxes with its own relaxation time. Alternatively, one can imagine that the supercooled liquid is homogeneous and each molecule relaxes identically in


Figure 3.4: Illustration of spatial heterogeneities near  $T_g$ . Diameter of the region is on the order of  $\xi_{het}$  and evolves with time t. (adapted from Ediger 2000 [3])

an inherently non-exponential manner [3]. The later explanation allows us to look at decreasing  $\beta$  with increasing cooperativity.

Spatially heterogeneous dynamics near  $T_g$  leads to non-exponential distribution of relaxation times in polymers. This non-exponential character, although not yet completely explored, may have profound influence on understanding transport properties and kinetics of chemical reactions in such materials.

# Jump diffusion model

As an implication of the non-Brownian spatially heterogeneous dynamics framework, some models look at the transport in glassy region as series of jump of the penetrant molecule from one position to the next. Probability of finding the penetrant molecule at a certain site is taken into account to calculate a frequency dependent diffusion coefficient D given by

$$D = \frac{1}{6} \frac{d^2}{\tau},\tag{3.9}$$

where d is the jump distance and  $\tau$  is residence time. Jump diffusion model oversimplifies the picture with a constant jump distance. No vibrational motion is taken in to account. It also overlooks the cage effect where the penetrant might be trapped at a site for a longer time and hence Equation 3.9 is equivalent to Fickian mean square displacement in long time [49]. Jump diffusion models can be used to model ionic transport in crystalline solids but a more rigorous approach is needed for polymer glasses [57, 58].

# Continuous Time Random Walk (CTRW) theory

This theory also assumes that penetrant is waiting at the site for a certain time  $\Delta t$  before jumping in to another site a distance  $\Delta r$  away.  $\Delta t$  and  $\Delta r$  are random variables and a waiting time distribution  $\psi(\Delta t)$  is assigned. This model is called *continuous time random walk* (CTRW) model. CTRW approach has been applied to model diffusion of ions in random medium [59–61]. Odagaki and Hiwatari have proposed using CTRW theory to predict gaussian to non-gaussian transition accompanied by glass transition [62, 63].

The non-Fickian character is usually attributed to slower relaxation dynamics in glassy polymers [2]. The classical Fickian assumption of free volume theory is only applicable when relaxation timescale in the polymer at experimental temperature is faster than the timescale of diffusive transfer [45].

# 3.3 Previous acid diffusion experiments

Acid diffusion leading to image blur has been a topic of research for researchers in this field since advent of chemically amplified resists. Several researchers have investigated different aspects of acid diffusion in photoresist, both above and below  $T_g$ . The approaches taken to measure diffusion coefficients can be classified in three major categories:

- 1. Single layer methods: These methods involve a single layer of polymer that undergoes a change in one of its properties. Examples include an uptake of a penetrant [64], or change in ionic conductivity of the film [65], or a reaction [66] involving the diffusing species inside the polymer layer.
- 2. Bilayer methods: The acid catalyst from a different layer (known as feeder layer) diffuses in to the polymer layer. The extent of deprotection is measured by different techniques [66–69] as a function of diffusion time and temperature, and that information is used to calculate the diffusion coefficient.
- 3. Trilayer methods: Acid from a feeder layer diffuses through an intermediate layer (layer of interest), and then arrives in a detector layer. The time required for travel through the intermediate layer is calculated. These data are used to calculate the diffusion coefficient.

#### 3.3.1 Single layer experiments

A popular method to measure diffusion in polymer films is through penetrant swelling experiments. A resist coated on Quartz Crystal Microbalance (QCM) crystal is placed in chamber where penetrant molecule can diffuse in the film. As penetrant diffuses in the film, its mass uptake is monitored by measuring the frequency of the QCM crystal. The mass uptake can then be related to diffusion coefficient of the penetrant in the film. Authors report a diffusion coefficient of the order of  $10^{-10}$  cm<sup>2</sup>/sec for diffusion of trifluoroacetic acid in 200 nm thick film of poly(hydroxystyrene) (PHOST) at 23°C [64]. An advantage of this method is it can be used to measure diffusion coefficient of inert molecule in an inert polymer matrix. Another method [65] involves measuring bulk ionic conductivity of the resist loaded with different concentrations of ionic species (acid catalyst) and using it in conjunction with Nernst-Einstein equation to calculate diffusion coefficient since acid catalyst is the major charge carrying species inside the film. A diffusion coefficient of  $4.3 \times 10^{-12}$  cm<sup>2</sup>/sec was calculated for triffic acid in PHOST ( $T_g$  170°C) at 23°C. Authors attribute such high diffusion coefficient values at room temperature to "dramatic effect" of relative humidity on ionic conductivity of the film both due to interaction between water and photoacid and the presence of water itself.

Kang et al. [66] have studied the deprotection of a single layer of model photoresist using FTIR spectroscopy. Various doses and post-exposure bake temperatures were used. The deprotection levels for changing times were calculated by using the drop in absorbance of the reacting species in the single layer. The data were modeled using acid catalyzed deprotection rate equations which models deprotection rate  $(K_P)$  and acid loss  $(K_T)$ . Authors assume no diffusion in single layer and defend the assumption by stating that acid loss factor incorporates both acid loss and diffusivity change.

Methods based on penetrant diffusion and ionic conductivity describe diffusion in standard Fickian form. A major limitation of first two methods, discussed above, is not being able to be carried out at lithographically relevant temperatures.

#### 3.3.2 Bilayer experiments

Bilayer experiments have an acid feeder layer either above or below the resist layer. After the acid activation and during the post exposure bake, acid diffuses in the resist layer, driving the deprotection reaction as shown in Figure 3.5. Data are analyzed through different means. For example, some studies immerse the sample in a "developer" that washes away part of the deprotected film. The amount of soluble film is assumed to be controlled by diffusion. Other approaches use infrared absorbance spectroscopy or neutron reflectivity to measure the composition after deprotection, and then interpret these data with a kinetic model.



Figure 3.5: Bilayer sample, with feeder layer on top, showing acid activation and post-exposure steps.

#### Bilayer with thickness measurement

Watanabe et al. [67] performed bilayer experiments where an acidic film of poly(acrylic acid) and ethylsulfonic acid was coated on top of polyvinylphenol (PVP) resin protected by tertbutoxycarbonyl (tBOC) groups. The bilayer was baked at 80°C and 90°C for various times. The films were then developed in TMAH solution and remaining thicknesses were noted. The thickness vs postbake times data was fit to a simple acid loss reaction model. Model assumes acid diffusion to be the rate limiting factor. The diffusion process is described by Fick's law. A first order acid reaction loss proportional to the concentration of the acid is also incorporated in the model. The diffusion coefficient in the deprotected region was found to be  $1.5 \times 10^{-13} \text{ cm}^2/\text{s}$  for 90°C post bake temperature.

#### Bilayer with reflectivity measurements

This method [68] requires a photoresist with deuterated protecting group. In this example, the resist is a copolymer of hydroxystyrene (HOST) and deuterated tertbutylacrylate (TBA). Once the acid catalyst has diffused through the P(HOSTco-TBA) layer during post exposure bake, neutron reflectivity measurements were performed. Deuterium provides a strong contrast between deprotected and protected regions of the resist. Analysis of reflectivity data yields the depth of the acid front propagation and hence deprotection extent in the resist. These deprotection profiles were then fit to a reaction-diffusion model based on first-order deprotection, acid catalyst trapping, and Fickian diffusion. Diffusion coefficients extracted from these length scales are  $1.3 \times 10^{-14}$  cm<sup>2</sup>/s for a PEB of 90°C for long-range front and vary from 0.15- $1.5 \times 10^{-16}$  cm<sup>2</sup>/s for short range front [70].

## Bilayer with infrared absorbance spectroscopy

This approach uses infrared (IR) absorbance spectroscopy to find out extent of deprotection. *Insitu* IR measurements are taken during the post exposure bake. An absorbance peak corresponding to protecting group is tracked with time and deprotection extent calculated by area under the peak. The data are then either fit to a coupled reaction-diffusion model or used to extract diffusion coefficient and activation energies from a stochastic kinetics simulator software [69]. Both approaches describe diffusion in standard Fickian form.

Modeling approach by Kang et al., along with coupled reaction-diffusion, also involves a trapping mechanism wherein acid catalyst may be trapped and rendered ineffective. The trapping rate is directly proportional to local photoacid concentration and extent of deprotection [66]. This approach gives an average diffusion coefficient of  $4.2 \times 10^{-14}$  cm<sup>2</sup>/s for P(HOST-co-TBA) films, in protected state, with thickness varying from 90-220 nm [71]. Post exposure bake temp is 90°C whereas  $T_g$  of the resin is 150°C. The latter stochastic simulations approach by Wallraff et al. [72] gives two different coefficients for protected poly((t-butoxycarbonyl)styrene) (PTBOCST) and deprotected (PHOST) regions. Diffusion coefficients for post exposure bake temperatures of 85°C are  $7x10^{-15}$  cm<sup>2</sup>/s and  $1x10^{-16}$  cm<sup>2</sup>/s for PTBOCST and PHOST respectively.

#### 3.3.3 Trilayer experiments

Main objective of trilayer experiments is to study diffusion in inert polymer films such as deprotected phase. An intermediate layer, the layer of interest, is sandwiched between an acid feeder layer and detector layer as shown in Figure 3.6. After the acid activation and during the post exposure bake step, the acid diffuses through the intermediate layer and finally reaches the detector layer. The detector layer is usually a polymer with acid-labile groups that undergo deprotection reaction catalyzed by acid. Onset of the acid in detector layer hence is indicated by reduction in absorbance of the acid-labile protecting group in IR. For example, in a commonly studied resin P(HOST-co-tBA), the tert-butyl moiety shows a reduction in its IR peak at 1150 cm<sup>-1</sup> as the deprotection progresses. The time required for acid arrival then is the time taken for the acid catalyst to diffuse through the film. A slope of the line of square of intermediate film thickness vs. time taken to diffuse gives the diffusion coefficient according to Fick's law.

Postnikov et al. [73] studied diffusion of nonaflate acid through poly(ethyl methacrylate) (PEMA) at temperatures above its  $T_g$  (68°C). PEMA is similar to PtBA but inert. It does not react with the diffusion acid. The diffusion coefficient for the nonaflate acid in PEMA at post exposure bake (PEB) temperature of 90°C was found to be  $3x10^{-12}$  cm<sup>2</sup>/s. The PEMA film thickness varied from 200 to 950 nm. For



Figure 3.6: Trilayer sample, with feeder layer on top, showing acid activation and post-exposure steps.

same nonaflate acid, using PMMA ( $T_g=126^{\circ}$ C) as intermediate layer gave a diffusion coefficient of  $6 \times 10^{-12}$  cm<sup>2</sup>/s at a temperature of  $123^{\circ}$ C [73]. The film thicknesses were varied from 225 to 765 nm. However, no diffusion was detected for PHOST ( $T_G$ ) films of thickness 135 and 600 nm at temperatures 70°C and 100°C, respectively, even after two days. Either PEB temperature was low or film thickness was so high that acid catalyst could not diffuse through the film even after carrying out the experiments for prolonged time. Using a diffusion coefficient of  $10^{-16}$  cm<sup>2</sup>/sec reported by Wallraff et al. [12], it will take about 10 days for an acid catalyst to diffuse through 135 nm film of PHOST at PEB temperature of  $85^{\circ}$ C.

Stewart et al. [4] carried out trilayer experiments to study the diffusion through PHOST at temperature from 5°C below to 15°C above  $T_g$  with film thicknesses varying from 300 to 1100 nm. These temperatures are well above post exposure bake temperatures used in lithography. The diffusion coefficient of the nonaflate acid through 510 nm thick PHOST film at 180°C (above  $T_g$ ) was found to be  $5 \times 10^{-13} \text{cm}^2/\text{s}$ . There was no acid arrival detected at temperature 160°C (below  $T_g$ ) [74].

# Chapter 4 Model chemically amplified resist

This section will introduce the system used for our deprotection studies- resins, photoacid generators, plasticizer, base quencher, and solvent. 2nd half of the chapter will discuss acid diffusion studies by other groups of this system.

# 4.0.4 Resin

We have used poly(hydroxystyrene-co-t-butyl acrylate) (P(HOST-co-tBA)) as polymer matrix for the deprotection and patterning studies. The chemical structure is shown in Figure 4.1(a). The polymer was provided by DuPont Electronic Materials. It is a random copolymer with 60 vol% HOST, molecular weight  $M_n = 10.4$ kg/mol and polydispersity index of 1.8. The glass transition temperature of this polymer is ~ 140°C. The copolymer is synthesized using 4-acetoxystyrene (ACOST) and



Figure 4.1: Structures of (a) P(HOST-co-tBA) and (b) P(S-co-tBA) resins.

benzoyl peroxide (BPO) monomers. The monomers are copolymerized in toluene for  $\sim 24$  hrs at 80°C to get random copolymers. After selective base hydrolysis step to convert ACOST to HOST, the polymer is precipitated out with acetic acid followed by purification in water, filtration, and drying steps [30].

P(HOST-co-tBA), apart from being a good ESCAP resin, provides uniform and

conformal films and thermal stability over a wide range of thicknesses and industrially relevant temperatures. It has been widely studied in industrial and research environments as representative ESCAP resin.

Another resin that we have used for our studies is poly(styrene-co-t-butyl acrylate) (P(S-co-tBA)). The structure can be seen in Figure 4.1(b). Its also a random copolymer with molecular weight  $M_n = 23.0$  kg/mol and polydispersity index of 2.1.

# 4.0.5 Photoacid generators (PAGs)

We have used two photoacid generators for our studies- triphenylsulfonium perfluoro-1-butanesulfonate (referred to as PFBS henceforth) (Mw = 562 g/mol) and triphenylsulfonium triflate (referred to as Tf henceforth)(Mw = 412 g/mol). Chemical structures are shown in Figure 4.2. Both were purchased from Sigma-Aldrich. Acid generation mechanism from the PAGs, after exposure to UV, will be discussed



Figure 4.2: Chemical structures of photoacid generators (a) PFBS and (b) Tf.

later in the chapter.

## 4.0.6 Plasticizer

Plasticizer was used to alter the dynamics of the resin and study its effect on deprotection behavior. We also measures glass transition temperatures of the films laced with plasticizer. We used dioctyl phthalate (DOP) (Mw = 390 g/mol) as the plasticizer for our studies. It was purchased from Sigma-Aldrich.

#### 4.0.7 Base quencher

Base quencher was used for acid generation studies where goal was to measure the acid generation efficiency of the PAGs. We used diphenylamine (DPA) as base quencher. It was purchased from Sigma-Aldrich as well. It has very low vapor pressure (1 mm Hg at 108°C).

#### 4.0.8 Solvent

Propylene glycol monomethyl ether acetate (PGMEA) (Sigma-Aldrich) was used as solvent to make all the formulas for our studies. It dissolves all the contents mentioned above over a wide range of concentrations. The boiling point of PGMEA is 145°C.

# 4.1 Deprotection reaction

Chemical amplification concept utilizes the gain mechanism due to ability of the acid catalyst to carry out hundreds of chemical transformations. While deprotection was one of the imaging mechanisms, chemical amplification was also used for other imaging routes like cross-linking for negative tone imaging [22] and depolymerization for self-developing positive tone resist [75]. The deprotection pathway was ultimately more successful and employed in manufacture of DRAM at IBM and hence gained a lot more attention.

Acid generation reaction for PFBS and subsequent deprotection reaction for our system are shown in Figure 4.3 and Figure 4.4, respectively. Lipophilic P(HOST-cotBA) is converted to a hydrophilic polymer by reaction with photochemically generated acid, which deprotects some of the tBA moieties to form acrylic acid.



Figure 4.3: Acid-counterion pair  $(H^+A^-)$  generation from PFBS after exposure to UV.

#### Specific acid catalysis

Deprotection reaction of P(HOST-co-tBA) is a well-known ester hydrolysis reaction where ester is catalyzed in presence of acid to form carboxylic acid and an alcohol. Ester hydrolysis occurs by either of the two pathways - specific acid catalysis and general acid catalysis. Deprotection reaction of our system (depicted in Figure 4.4) occurs through specific acid catalysis pathway. The proton generated binds to the protective pendant group on the polymer backbone, which in turn induces fragmentation to generate the deprotected product, carboxylic acid and an unstable carbocation. This carbocation releases a proton and which is then available for next deprotection event [76]. A simpler version of this reaction is shown below.

$$S + HA \rightleftharpoons SH^+ + A^-$$
 Fast  
 $SH^+ \rightarrow products$  Slow

Ester (S) forms a protonated complex  $(SH^+)$  with acid in a rapid equilibrium step followed by a slower product forming step. Concentration  $[SH^+]$  determines the overall rate of deprotection, which in turn depends on acidity of HA (ability to donate a



Figure 4.4: Overall deprotection reaction where  $H^+A^-$  denotes acid-counterion pair.

proton) and basicity of S (ability to accept the proton). Acid catalysts used in CA resists are usually strong acids (for example, Tf  $pK_a = -12$ ) and care has to be taken to avoid any airborne basic contaminants from interfering with the reaction.

It has to be noted that specific acid catalysis mechanism described above applies for solution phase. If such a reaction were to be carried out in solid polymer glass, where molecular mobilities are heavily reduced, encounter rates of reactants, activated complex orientations, and degassing (escaping from the medium) of the byproducts are going to play a significant role in determining rate limiting step.

#### 4.1.1 Previous studies of this system

#### **Reaction limited approach**

Hinsberg et al studied the Poly(tert-butoxycarbonyloxystyrene) (PTBOCST), a structurally similar positive tone CA resist. [76–78] The acid counterion used was PFBS. They measured the bulk deprotection kinetics by infrared spectroscopy. Experimental data were used to extract parameters by assuming kinetics are reaction controlled i.e. controlled by step 2 in Figure 4.4. These reactions for this particular system are shown below -

$$PTBOCSTH^{+} + PHOST \rightleftharpoons PTBOCST + PHOSTH^{+}$$
Fast
$$PTBOCSTH^{+} \rightarrow PHOSTH^{+}$$
Slow

For PTBOCST, Arrhenius parameters for the rate constant of rate determining step were  $A = 1.4 \times 10^{18} \text{ sec}^{-1}$  and  $E_a = 120 \text{ kJ/mol}$  [78]. The PEB temperatures used were 45-65°C to minimize any thermal deprotection.

# Diffusion limited approach

The details of acid transport were extracted by comparing experimental behavior of diffusion of acid from a layer on top of the CA resist layer during post exposure bake process to that predicted by a model that uses Fickian diffusion coefficient as the only parameter [79]. This is explained in Figure 4.5. Authors used two different diffusion coefficients for protected and deprotected regions since deprotected polymer is more polarized and may slow down acid (an ionic species) diffusion. Diffusion coefficients and activation energies for protected (TBOCST) and deprotected (HOST) polymers reported by Hinsberg and co-workers [76] and for P(HOST-co-tBA) reported by Kang and co-workers [9] are reported in Table 4.1. All the models use Fick's law to model



Figure 4.5: Simulation approach used by Hinsbeg and co-workers to model acid tranport. Resist is represented as a stack of homogenous slabs with diffusion occuring between the layers described Fickian kinetics.

tranposrt of acid from an acid reservioir layer to a protected polymer film. These diffusion coefficient result in an effective acid diffusion length of 5 nm for a PEB temperature of 100°C and PEB time 120 sec.

Polymer	Temp (°C)	$D imes 10^{-14}\ ({ m cm}^2/{ m sec})$	$A~({ m cm^2/sec})$	$E_a \ ({ m kJ/mol})$
PTBOCST [76]	65-105	0.15-15	$1.9 \times 10^{8}$	153
PHOST [76]	65-105	0.004-0.1	$9 \times 10^{-3}$	92
P(HOST-co-tBA) [9]	60-100	4.2	$44 \times 10^{-14}$	127

Table 4.1: Diffusion coefficients and activation energies

Another group from NIST [9] studied P(HOST-co-tBA) resin (PHOST 50 mol%) and PFBS counterion. Experimental deprotection rates were measured using IR spectroscopy. Data were modeled using a coupled reaction-diffusion model. The model is described in Equations (4.1) to (4.3),

$$H = [PAG](1 - e^{-CE}),$$
 (4.1)

$$\frac{d\phi}{dt} = k_P H (1 - \phi), and \tag{4.2}$$

$$\frac{\partial H}{\partial t} = D_H \nabla^2 - k_T H \phi. \tag{4.3}$$



Two types of systems used by Kang and co-workers to study reaction and diffusion.(a)

Figure 4.6: Two types of systems used by Kang and co-workers.

Fully deprotected single layer system shows PAG and resist in the same layer where there is no gradient of acid catalyst. This layer is used to extract  $K_P$  and  $K_T$ ,  $(D_H = 0).(b)$  Bilayer system with a PAG + resist layer on top of PAG-free layer where extent of deprotection is limited by diffusion of the photoacid in the bottom layer. Top layer is fully deprotected and bottom layer is partially deprotected. Bilayer studies are used to extract all three paramteres-  $K_P$ ,  $K_T$ , and  $D_H$ . These systems are shown in Figure 4.6. The output parameters are reaction rate constant  $(k_P)$ , a trapping rate constant  $(k_T)$ , and a diffusion constant  $(D_H)$ . Deprotection rate depends on local acid concentration and extent of deprotection. Acid concentration change is given by Fickian diffusive flux combined with an acid loss term. Stoichiometric acid loss is proportional to local acid concentration and level of deprotection. Authors report an average diffusion coefficient of 4.2 x 10<sup>-14</sup> cm<sup>2</sup>/sec at PEB temperature of 90°C for a bilayer model where acid diffuses in to the CA resist layer from a different later on top of it (reported in table 4.1). Table 4.2 shows Arrhenius parameters for  $k_P$ ,  $k_T$ , and  $D_H$ .

As an important conclusion of their work, from their bilayer experiments, authors observe that the deprotection is governed by diffusion of acid since deprotection in

Reacti	on rate	Photoacid <sup>·</sup>	trapping	Diffusion	coefficient
$\operatorname{constant}$	$({ m nm^3/sec})$	constant $(s^{-1})$		$(nm^2/sec)$	
$\ln k_P = A$	$-E_a/RT$	${ m ln}k_T=A$ -	$-E_a/RT$	$D_H = A$ ex	$\exp(-E_a/RT)$
Δ	$E_a$	Δ	$E_a$	A	$E_a$
Л	(kJ/mol)	Л	(kJ/mol)	$(\rm nm^2/sec)$	(kJ/mol)
$45 \pm 1$	$136 \pm 3$	$25\pm2$	$86 \pm 5$	$44 \pm 8$	$127 \pm 25$

Table 4.2: Arrhenius parameters for reaction and diffusion constants [9].

a single layer (no acid gradient) was consistently higher than a bilayer. This is also supported by the fact that they find activation energies of reaction and diffusion closer to each other (Table 4.2).

# Chapter 5 Bulk deprotection experiments

# 5.1 Introduction

Chemically amplified (CA) resists are a class of lithographic materials that enable high-throughput semiconductor patterning. These systems are comprised of a glassy polymer film loaded with a photoacid generator (PAG). Patterns are formed by using light to activate a strong acid catalyst in localized regions, and then heating the film at moderate temperature to promote acid diffusion coupled to polymer "deprotection." The deprotection reaction changes the polymer's polarity for a subsequent development step, so the more soluble regions of the polymer are selectively washed away.

CA resists have been studied for more than 30 years, and it is well-established that deprotection kinetics is controlled by acid diffusion. However, experimental data are inconsistent with a first-order reaction coupled to Fickian transport, and the physics and chemistry that drive this unusual behavior are unknown. Semiconductor lithography is striving to achieve 10 nm resolution, so there is significant demand for quantitative models that predict acid translations with nanoscale spatial resolution. As a first step towards this goal, we recently studied reaction kinetics in a model CA resist using infrared absorbance spectroscopy and spatially-resolved stochastic simulations [80,81]. Experimental data were interpreted with a simple and efficient model based on subdiffusive acid transport coupled to a phenomenological acid loss. The model predicted key aspects of the macroscopic deprotection rates, such as fast reaction at short times, slow reaction at long time, and a nonlinear dependence on acid loading. However, while the model offered near-quantitative agreement with experiments, the underlying cause(s) of anomalous acid transport remain unclear. It is widely accepted that polymer glasses are characterized by spatial heterogeneities in dynamics, which is detected in experiments through non-exponential relaxation processe [?,3]. There are very few studies that have linked such behavior to anomalous translational diffusion, [82,83] perhaps due to the challenge of measuring nanoscale displacements with any accuracy. In our previous work, the rate of deprotection served as an indirect "reporter" of acid motion, and we demonstrated anomalous behavior through modeling rather than a direct measurement. In this work, we systematically vary the coupling between acid transport and polymer dynamics, effectively tuning the sensitivity of our experiments to dynamic heterogeneities in the system. The outcomes can elucidate the effects of glassy physics on reaction propagation in CA resists.

First, we note that photolysis of the PAG will produce a strong acid and counterion. As the resist is heated, the acid and counterion will diffuse together to maintain electroneutrality. The translational diffusion rate of small molecules in glassy polymers is very sensitive to the structure of the diffusant, the strength of diffusant/polymer interactions, and dynamical properties of the polymer. Diffusivities at  $T_g$  can span a broad range from  $10^{-12}$  cm<sup>2</sup>/sec to  $10^{-16}$  cm<sup>2</sup>/sec, where the slowest rates are observed when the diffusants are large, [84,85] or in systems with attractive secondary interactions between diffusant and polyme [86,87]. These trends reflect the strong coupling between penetrant mobility and polymer relaxation dynamics. Many studies of glassy CA resists have aimed to capture the effects of acid-counterion structure on diffusion lengths and image resolution. Measurements of pattern line widths [88] and ionic conductivity [89] indicate that diffusion rates are suppressed with large, bulky anions. Neutron reflectivity in model bilayer resists can the shape of the reaction front along one dimension, and these data show that larger anions have shorter diffusion lengths and generate a sharper deprotection profile [90]. With this knowledge in mind, we measure deprotection kinetics as a function of anion size, with the expectation that larger anions will be more sensitive to glassy dynamics, and therefore exhibit greater deviations from Fickian behavior.

Second, plasticizer additives are often used to tune the dynamical properties of glassy polymers. As examples, plasticizers can suppress the glass transition  $(T_g)$ , [91,92] minimize the effects of confinement on  $T_g$ , [93] reduce the breadth of segmental relaxation times, [94,95] and produce faster relaxation dynamics [94–96]. Studies have shown enhanced rates of penetrant diffusion in plasticized glassy polymers [97,98]. Therefore, we measure deprotection kinetics in resists with 0 or 10 wt% plasticizer, and anticipate that formulas containing plasticizer will exhibit faster transport rates with less anomalous character.

# 5.2 Experimental Procedures

# 5.2.1 Materials

The polymer resin used for these studies was a random copolymer poly(hydroxystyreneco-tertbutyl acrylate), abbreviated as P(HOST-co-tBA), with 60 vol% HOST, molecular weight of  $M_n = 10.4$  kg/mol, and dispersity of 1.8 (DuPont Electronic Materials). Two types of photoacid generator (PAG) were employed: triphenylsulfonium perfluorobutanesulfonate (PFBS) and triphenylsulfonium triflate (TPS Tf) (Sigma-Aldrich). Dioctyl phthalate (DOP) was used as a plasticizer (Sigma-Aldrich). The vapor pressure of DOP is 1.2 mm Hg at 93°C. Diphenylamine (DPA) was used as a base quencher for measurements of acid generation efficiency (Sigma-Aldrich). DPA has a vapor pressure of 1 mm Hg at 108°C. All resist formulas were prepared by adding copolymer, PAG, DOP and DPA to the solvent propylene glycol monomethyl ether acetate (PGMEA, Sigma-Aldrich). The developer was MF-319 (MicroChem), which is an aqueous 0.26N tetramethylammonium hydroxide (TMAH) solution. MF-319 was diluted with deionized water to 0.1N for our experiments. Substrates used for measurements of acid generation efficiency and for nanopatterning were single-side polished p-type (100) silicon (standard resistivity). Substrates for infrared absorbance spectroscopy were double-side polished p-type (100) silicon with high resistivity (>6000 Ohm-cm). Silicon substrates were cleaned by immersing in Piranha bath (20 vol% hydrogen peroxide, 80 vol% sulfuric acid) for 6 min (CAUTION! Piranha bath is extremely corrosive and incompatible with organic materials). Piranha bath destroys organic contamination and grows a thin oxide layer that is extremely hydrophilic.

## 5.2.2 Extinction Coefficient

The extinction coefficient of the P(HOST-co-tBA) resin was measured as a function of wavelength with a J.A. Woollam M-2000 spectroscopic ellipsometer ( $\lambda = 190$  nm - 1690 nm). The angle of incidence/detection was 70°. The refractive index of the films was described by the Cauchy dispersion model  $n(\lambda) = A + B/\lambda^2$  with an Urbach tail [99] to capture absorption in the deep ultraviolet range. The Urbach model has the form  $\kappa(E) = A_{\kappa} \exp[B_{\kappa}(E - E_b)]$ , where  $E = hc/\lambda$  is the photon energy and  $E_b$  is the energy at the band edge. The parameters  $A, B, A_{\kappa}, B_{\kappa}$ , and film thickness were adjustable parameters for regression analysis.

## 5.2.3 Acid Generation

The efficiency of acid generation was calculated using the standard addition technique proposed by Dill [100–102]. Five resist formulas were prepared for each type of PAG that contained different DPA-to-PAG molar ratios: 0 (no base quencher), 0.25, 0.5, 0.75, 1. Resist films with thicknesses of  $(300\pm20)$  nm were prepared by spin-casting on silicon. Films were exposed to 254 nm UV light (1.5 mW/cm<sup>2</sup>) for times up to 2 mins, leading to a delivered dose up to 45 mJ/cm<sup>2</sup>. After exposure, each film was

baked at 90°C for 30 sec, and then films were immersed in developer (0.1N TMAH) for 20 sec. (The un-exposed resist is insoluble in the developer.) The film thicknesses before  $(h_0)$  and after  $(h_t)$  development were measured with a J.A. Woollam M-2000 spectroscopic ellipsometer ( $\lambda = 350$  nm - 1690 nm). The angle of incidence/detection was 70°. The refractive index of the films was described by the Cauchy dispersion model  $n(\lambda) = A + B/\lambda^2$  where A, B, and thickness were adjustable parameters for regression analysis (all positive values). Typical values of A and B were 1.5 and 0.005, respectively. The normalized residual thickness  $(h_t/h_0)$  was plotted against the corresponding dose for each formula (Figure 5.1a-b), and the critical dose  $E_0$  was determined by the point where the entire film was washed away such that  $h_t/h_0=0$ . The critical dose was then plotted against the DPA:PAG molar ratio (Figure 5.1c-d), and the Dill C parameter was calculated from the slope of a linear fit,

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

where a is the film absorbance (base e). The absorbance a was calculated from  $a = \alpha \ln(10)h_0$ . The absorption coefficient is  $\alpha = 4\pi\kappa/\lambda$ , where  $\lambda$  is the wavelength of the UV light (254 nm) and  $\kappa = 0.011$  is the extinction coefficient of the resist at 254 nm. The Dill C parameter is  $0.039 \pm 0.007 \text{ cm}^2/\text{mJ}$  for PFBS and  $0.073 \pm 0.014 \text{ cm}^2/\text{mJ}$  for Tf.

#### 5.2.4 Sample Preparation

Resist formulas were prepared by dissolving 10 wt% polymer resin in PGMEA. PAG was added to the solution at loadings of 1, 2, or 4 wt% relative to the polymer. DOP plasticizer was added to some formulas at a loading of 10 wt% relative to the polymer. Typical contents of a formula are summarized in Table 5.1. Base quenchers were not employed for any studies of deprotection kinetics.



Figure 5.1: Determining acid generation efficiency with Dill's method. Contrast curves for PFBS (a) and Tf (b). Best-fit lines to calculate Dill C parameter for PFBS (c) and Tf (d) in units of cm<sup>2</sup>/mJ. The dashed curves in (a) and (b) are drawn to guide the eyes and are not fits to the data.

Table 5.1: Contents of a formula

Polymer resin Acid ture $(\mathbf{D}\mathbf{A}\mathbf{C})$	P(HOST-co-tBA)
Acid type (PAG) Acid loading	1, 2, or 4 wt % (relative to polymer)
Plasticizer	0 or 10 wt % DOP (relative to polymer)

Resists were spin-coated on double-side polished silicon wafers to produce film thicknesses in the range of 280 nm - 320 nm. Films were soft-baked at 130°C for 2 min to drive out residual PGMEA solvent. Films were then exposed to UV light ( $\lambda$ = 254 nm) with an intensity of 1.5 mW/cm<sup>2</sup>, and the exposure time was set to 90 sec for a dose of 135 mJ/cm<sup>2</sup>. Acid generation efficiency is calculated by the formula,

$$[\mathrm{H}^+] = [\mathrm{PAG}]_0 [1 - \exp(-CD)], \tag{5.2}$$

where D is the dose delivered to the film. Using the Dill C parameters for PFBS and

Tf, we predict that more than 99% of either acid is activated with this process. The wafer is then split into several smaller pieces, and each piece is baked for different times (ranging from 5 sec to several hr) on a shielded hot plate to vary the extent of deprotection. The reaction temperatures used for these experiments were 70°C, 80°C, and 90°C. The same protocols were used for all resist formulas.

#### 5.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

IR absorbance was measured with a Nicolet NEXUS 670 FTIR spectrometer equipped with a Brewster angle sample stage. Samples were measured at an incident angle of 16° which is the Brewster angle for the silicon substrate. IR data were recorded at a resolution of 8 cm<sup>-1</sup> with an average of 128 scans using OMNIC data acquisition software. The baseline was subtracted using a "point and click" approach in Matlab, where a user identifies the minima in the spectra and software fits a line to connect those points. The signal from a plain silicon wafer is subtracted from each copolymer spectrum. Table 5.2 summarizes the relevant peaks in the IR spectrum and their assignments. [103]

Table 5.2: Key IR peak assignments for P(HOST-co-tBA)

Wavenumber $(cm^{-1})$	Assignment
1393, 1369	CH <sub>3</sub> split umbrella mode of <i>tert</i> -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

The strongest peak associated with tBA is detected at 1149 cm<sup>-1</sup>, so this signal is used to evaluate deprotection kinetics. 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 cm<sup>-1</sup>, 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 reaction times. Examples of these data are reported in Figure 5.2.



Figure 5.2: IR absorbance data for P(HOST-co-tBA) resist with 1 wt% Tf and 10 wt% DOP, deprotected at 80°C. The peak at 1149 cm<sup>-1</sup> is associated with C-O-C stretches of tBA moieties.

Within each series of measurements, the peak widths at 1149 cm<sup>-1</sup> (Gaussian) and 1172 cm<sup>-1</sup> (Lorentzian) were constrained at a constant value that reflects the best-fit to the entire data set, so the shape of the peaks did not change with reaction time. Typical widths are 8 cm<sup>-1</sup> at 1149 cm<sup>-1</sup> (Gaussian) and 25 cm<sup>-1</sup> at 1172 cm<sup>-1</sup> (Lorentzian). The deprotection level ( $\phi$ ), or extent of reaction, was calculated from the ratio of final-to-initial tBA absorbance and corrected for thickness change during the reaction,

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

where  $[tBA_f]$  is the final absorbance of a sample with thickness  $h_f$ , and  $[tBA_0]$  is the absorbance of the initial unreacted sample with thickness  $h_0$ . The uncertainty (95% confidence interval) was determined by performing multiple measurements per sample and its value is 3% for  $\phi < 0.85$  and 5% for  $\phi > 0.85$ . Higher uncertainty is seen when  $\phi \to 1$  since the tBA signals are weak.

## 5.2.6 Glass Transition Temperature

Films were prepared as previously described, but without exposure to UV light so the catalyst (when present) was not activated. We used a J.A. Woollam M-2000 ellipsometer ( $\lambda = 350 \text{ nm} - 1690 \text{ nm}$ ) equipped with an Instee HTC-200 heat cell to measure changes in film thickness as a function of temperature. The h(T) curves exhibit two slopes due to the discontinuous change in thermal expansion for a glass and melt [104]. The cell was purged with nitrogen gas (0.4-0.6 scfh) to maintain an inert atmosphere. The angle of incidence/detection was 70°. Samples were heated at a constant temperature of 130 °C for 10 min to drive out residual solvent before commencing the T<sub>g</sub> measurement. Three heating and cooling cycles were implemented over the temperature range of 130-160°C at a rate of 2 or 2.6 K/min. The refractive index of the films was described by the Cauchy dispersion model  $n(\lambda) = A + B/\lambda^2$  where A, B, and thickness were adjustable parameters (all positive values). We measured three formulas: Plain resin, resin with 4 wt% PFBS, and resin with 1 wt% PFBS and 10 wt% DOP. The film thicknesses were (300 ± 20) nm in all cases.

# 5.3 Simulation Methods

Following methods reported elsewhere, [80] experimental data were analyzed with stochastic simulations implemented on a three-dimensional lattice  $(1 \text{ nm}^3/\text{cell})$ . At the start of the simulation (t = 0), each cell represents a region of protected P(HOST-co-tBA) resin, and acid catalysts (phantom particles) are randomly distributed throughout the lattice at a specified volume concentration. Acid translations were described with the mathematical formalism of a continuous time random walk (CTRW) based on a non-ergodic, non-Markovian process that models sub-diffusive behavior. This algorithm selects waiting time intervals  $(t_{\Delta})$  for acid hopping from the Pareto probability density:

$$\Psi(t_{\Delta}) = \frac{\gamma/\tau}{\left(1 + t_{\Delta}/\tau\right)^{(1+\gamma)}}.$$
(5.4)

Many studies have demonstrated that reaction and byproduct volatilization are rapid events compared with acid diffusion. Therefore, when an acid translates into a protected cell, deprotection and byproduct volatilization events are assumed to be instantaneous. To describe the apparent self-limiting behavior at long times, we introduced a simple acid loss mechanism where an acid molecule is deactivated if it hops into an occupied lattice site:

$$\mathrm{H}^{+} + \mathrm{H}^{+} \to \mathrm{H}^{+}. \tag{5.5}$$

This phenomenological annihilation process does not introduce any unknown parameters.

The characteristic diffusion time  $\tau$  and anomalous exponent  $\gamma$  are the only unknown model parameters, and their values depend on the reaction temperature, anion size, and plasticizer loading. We used a simulated annealing optimization algorithm to find pairs of  $\tau$  and  $\gamma$  that best describe each experimental data set. Each function evaluation in the algorithm proposes values for  $\tau$  and  $\gamma$ , generates an initial distribution of acid catalyst, performs the simulation, and then compares predicted and measured deprotection profiles ( $\phi(t)$ ). A minimum of 50 runs were performed for each data set on a 30 × 30 × 30 lattice. Each run cycles through high and low "temperatures", with 200 move attempts per temperature, and proposed changes in  $\tau$  and  $\gamma$  are accepted or rejected based on the Metropolis criterion. This procedure requires many hundreds of function evaluations, so a simple and efficient model of acid diffusion is critical to the success of this approach.

Each experimental data set includes deprotection profiles  $\phi(t)$  for three acid

concentrations (1 wt%, 2 wt%, and 4 wt%). To reduce the simulation time, the profiles for each acid concentration were projected onto a master curve for 1 wt%. The 50+ runs yielded many pairs of  $\tau$  and  $\gamma$  that could describe the 1 wt% data. As a final step, we simulated deprotection profiles for each pair of model parameters at acid concentrations of 1 wt%, 2 wt%, and 4 wt% on a lattice of 50 × 50 × 50 cells. A small subset of similar { $\tau, \gamma$ } pairs captured the observed scaling of deprotection rate on acid loading.

# 5.4 Results

**System.** The overall acid-catalyzed deprotection reaction for P(HOST-co-tBA) is illustrated in Figure 5.3a: tBA moieties are cleaved by acidolysis to produce acrylic acid and volatile isobutylene byproduct. We examined four systems based on the P(HOST-co-tBA) resin: Two different counterion sizes (Figure 5.3b-c), with and without 10 wt% of the plasticizer DOP (Figure 5.3d). For each resist formula, the extent of deprotection ( $\phi$ ) was measured as a function of time at 70°C, 80°C, and 90°C using acid loadings of 1 wt%, 2 wt%, and 4 wt%.



Figure 5.3: (a) Overall deprotection reaction with acid-counterion H<sup>+</sup>X<sup>-</sup>. (b) PFBS counterion. (c) Tf counterion. (d) Plasticizer (DOP).

The glass transition temperature of each resist formula was determined by measuring the film thickness as a function of temperature [105]. The discontinuity in thermal expansion marks the transition from a glass to a melt and is marked by the arrow in Figure 5.4.  $T_g$  values are calculated from the average of three cooling cycles (Table 5.3). Inclusion of additives such as PAG and DOP does not alter the  $T_g$  value of the P(HOST-co-tBA) resin. This is a surprising result, as additives will typically reduce  $T_g$  in bulk polymers or films [93, 106]. The important conclusion of these experiments is that all deprotection reactions are implemented at temperatures well below the  $T_g$  of the polymer reactant, so models of deprotection kinetics should reflect the physics of a polymer glass.



Figure 5.4:  $T_g$  measurement P(HOST-co-tBA) film with 1 wt% PFBS and 10 wt% DOP. (Cooling cycle.)

Table 5.3:  $T_g$  values of P(HOST-co-tBA) formulas.

PAG	DOP	$T_g$ (°C)
None	0  m wt%	$149.2 \pm 1.5$
$4 \mathrm{wt}\% \mathrm{PFBS}$	$0  \operatorname{wt}\%$	$148.6 {\pm} 1.1$
$1 \mathrm{wt}\% \mathrm{PFBS}$	$10~{\rm wt}\%$	$148.2 \pm 1.5$

**Reaction Kinetics.** The acid-catalyzed deprotection of P(HOST-co-tBA) is expected to follow first-order kinetics [76, 79] as described by Equation 5.6,

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = k[\mathrm{H}^+]^n (1-\phi). \tag{5.6}$$

where  $[\mathrm{H}^+]$  is the acid concentration and  $\phi$  is the extent of deprotection ( $0 \leq \phi \leq$  1). This implies that deprotection rates should scale linearly with acid concentration. However, our experiments exhibit a stronger-than-linear dependence on acid concentrations, so the rates increase as  $[\mathrm{H}^+]^n$  with n > 1. This is demonstrated by the example in Figure 5.5, where data for three different acid concentrations are collapsed on a master curve that reflects an apparent reaction order of n = 1.2. For example, the time data for 4 wt% loading was multiplied by  $4^{1.2}$ , which superimposes these points onto the 1 wt% curve. The solid line is the analytic solution to Equation 5.6. Clearly, a simple first-order rate law cannot capture the deprotection kinetics in these systems.



Figure 5.5: Master curve for Tf with 10 wt% DOP and reaction temperature of 90°C. Solid line reports the best-fit to a first-order reaction (Equation 5.6).

Figure 5.6 summarizes the apparent order n for all resist formulas, and there are several interesting trends: First, n decreases with increasing temperature. Second, ndecreases with reduced counterion size, although this trend vanishes at the highest temperature considered. Finally, n decreases when DOP is added to either formula. These observations suggest that deviations from first-order kinetics are at least partly associated with dynamical properties in the polymer resin, which is further discussed in later sections of this chapter.



Figure 5.6: Apparent order n as a function of temperature for each resist formula.

Several literature studies have described similar deviations from first-order kinetics [80, 107–109]. Recent work from Thompson, Ober, and co-workers offers insight into the underlying physics and chemistry that drive this behavior [108-110]. The authors compared conventional processing on a hotplate with sub-millisecond high-temperature laser annealing, so the reaction temperatures ranged from below to well-above the polymer's glass transition. At low temperatures, the apparent reaction order was either  $n \approx 2$  or  $n \approx 4$  depending on the type of polymer resin, while at high temperatures it approached  $n \approx 1$ . This behavior was initially attributed to diffusion-controlled kinetics at low temperature and reaction-controlled kinetics at high temperature [109]. A later publication revealed a competing pathway of acid-catalyzed byproduct dimerization at low temperature, and this mechanism is consistent with an apparent reaction order n > 1 [110]. In our prior work, [80] we demonstrated that non-Fickian diffusion at low temperatures could explain an apparent reaction order of n > 1 and quantitatively describe deprotection rates at short times. However, a slow acid loss was needed to describe deprotection rates at long times.

**Non-Fickian Diffusion.** The model we employ to analyze macroscopic kinetics is based on diffusion-controlled deprotection coupled to a slow side reaction that depletes acid catalyst [80]. The unique attribute of this model is a non-Fickian acid transport process that can account for the coupling between glassy polymer dynamics and acid mobility. The model parameters that describe the non-Fickian behavior are a characteristic timescale  $\tau$  and an anomalous exponent  $\gamma < 1$ .

We optimized the values of  $\tau$  and  $\gamma$  to achieve near-quantitative agreement between experiments and simulations at all acid concentrations. As an example, Figures 5.7a and 5.7b compare measured deprotection rates in each formula at 70 °C with the optimized simulation outcomes. Two trends are visible to the eye: First, the rate of deprotection in each formula is enhanced by addition of plasticizer, where this effect is particularly pronounced for the larger PFBS anion. Second, the rate of deprotection appears to be much faster with the small Tf anion compared with the bulkier PFBS anion. The volume concentration of Tf is approximately 28% higher than PFBS at a fixed weight percent, so the actual difference in rates is not as extreme as it appears in Figure 5.7.

Figure 5.8 reports the time required for 50% deprotection in each resist formula as a function of temperature and acid loading. Experimental data are compared with the outcomes of optimized simulations, and we observe excellent agreement in (nearly) all cases. (The aberration for PFBS formula at 1 wt% acid loading is also observed in Figure 5.7b. We suspect that acid was deactivated over the very long timescale by accidental environmental contamination.) The trends observed at 70 °C in Figure 5.7 hold for all temperatures: The time required to achieve 50% deprotection is reduced by the addition of plasticizer or by decreasing the size of the anion, and plasticizer has a bigger impact on deprotection rates for the larger PFBS anion. Furthermore, the kinetics in each formula is consistent with an Arrhenius temperature dependence.

Figure 5.9 reports the optimized model parameters as a function of temperature for each formula. The parameter  $1/\tau$  represents the characteristic macroscopic rate



Figure 5.7: Measured deprotection rates with best-fit to the anomalous diffusion model. Open/closed symbols designate resists with/without DOP. (a) Tf counterion at 70°C; (b) PFBS counterion at 70°C. Inset plot reports the residuals.

of diffusion. The activation energies for acid diffusion in each formula were determined from the Arrhenius temperature dependence, i.e.,  $\ln[1/\tau] \propto -E_a/RT$ , and are reported in Table 5.4 with statistically-derived uncertainties. The values of  $E_a$  for each formula are on the order of 100 kJ/mol, and are consistent with other studies of acid diffusion in CA resists [9]. Similar activation energies are reported for diffusion-controlled kinetics in solid state polymerization [111]. The anomalous exponent  $\gamma$  captures the deviations from Fickian behavior. We note that mean-squared



Figure 5.8: Times required for 50% deprotection as a function of temperature and acid loading. Experiments are compared with the optimized simulations for each formula: (a) Tf, (b) Tf + DOP, (c) PFBS, (d) PFBS + DOP.

acid displacements in our transport model follow the scaling,

$$\langle x^2(t) \rangle \propto t^{\gamma}.$$
 (5.7)

We find that  $\gamma$  is always less than 1, but increases as we raise temperature, add plasticizer, or reduce acid-anion size.

The anomalous diffusion model predicts a distribution of acid hopping times in the system, meaning there are "fast" and "slow" regions of the polymer films. This description is consistent with the stretched exponential dynamics that are observed



Figure 5.9: (a) Characteristic diffusion rate  $1/\tau$  as a function of temperature. (b) Anomalous exponent  $\gamma$  as a function of temperature. Note that  $\gamma < 1$ reproduces subdiffusive transport, while  $\gamma = 1$  represents Fickian transport.

in many systems of soft condensed matter, [112] including glassy polymers [113]. In the context of our work, the parameter  $\gamma$  reflects how strongly the acid transport is coupled to heterogeneous glassy dynamics. Any diffusive process should approach Fickian behavior in the long-time limit,

$$\lim_{t \to \infty} \langle x^2(t) \rangle = 6Dt, \tag{5.8}$$

so it is difficult to validate anomalous transport through experiments, as there are few techniques that can probe the nanoscale displacements at short times. We are aware

Formula	$E_a ~({ m kJ/mol})$
Tf	$127 \pm 19$
PfBS	$138 \pm 11$
$\mathrm{Tf} + \mathrm{DOP}$	$130 \pm 11$
PFBS + DOP	$116\pm7$

Table 5.4: Activation energies for acid diffusion  $(E_a)$ .

of only one study that measured translational motion of small molecules in a glassy polymer, [82,83] and the authors found  $\gamma = 0.8$  with  $\langle x^2(t) \rangle^{1/2}$  on the order of 10 nm. We determined similar values of  $\gamma$  in our experiments, and we predict  $\langle x^2(t) \rangle^{1/2}$  less than 20 nm at the longest times and highest temperatures, [80, 81] which supports the validity of our modeling approach. If acid transport is controlled by glassy dynamics, then we can anticipate certain trends in  $\gamma$  and  $\tau$  as a function of temperature, anion size, and plasticizer loading. First, cooling will broaden the distribution of polymer relaxation times, which is manifested in our model as a reduction in  $\gamma$ . Cooling will also suppress the rate of a thermally-activated transport process, so  $\tau$   $(1/\tau)$  will decrease (increase) following the Arrhenius law. We observe both of these behaviors, although trends in  $\gamma$  are partially obscured by the uncertainty of the analysis. We note that studies of polymer relaxation dynamics do not detect large changes in  $\gamma$ with small changes in temperature, except when the system is near  $\mathcal{T}_g$  [113]. Second, the coupling between transport and segmental motion increases with the diffusant size, [84, 85] so the PFBS anion should exhibit smaller values of  $\gamma$  and  $\tau$  than the Tf anion. We find that  $\gamma$  scales as expected, but differences in  $\tau$  for each anion are difficult to discern. (Note that the diffusion is controlled by both  $\gamma$  and  $\tau$ , so it is technically incorrect to state that  $\tau$  alone captures the characteristic rate. We are working on a more rigorous analysis to address this issue.) Finally, plasticizers will narrow the distribution of relaxation times, shifting  $\gamma$  closer to 1, and they will also produce faster relaxation dynamics, thereby reducing  $\tau$  [94–96]. We observe both of
these trends in PFBS formulas. However, only  $\tau$  scales as expected in Tf resists, while  $\gamma$  is nearly invariant with plasticizer loading.

## 5.5 Conclusions

We examined the effects of temperature, acid-anion size, and plasticizer concentration on deprotection kinetics in CA resists. Macroscopic deprotections rates were measured with IR spectroscopy, and data were interpreted with a simple and efficient model of subdiffusive acid transport. We found an apparent reaction order n > 1 in all formulas, and the limit  $n \rightarrow 1$  was approached with increasing temperature, reduced anion size, and plasticized resists. The diffusion timescale extracted from simulations  $(\tau)$  exhibits an Arrhenius temperature dependence with an activation energy on the order of 100 kJ/mol, which is consistent with other studies of diffusion-controlled kinetics in glassy polymers. The diffusion rate is significantly enhanced by addition of plasticizer, and weakly enhanced by reduced anion size. Subdiffusive character is captured by the exponent  $\gamma < 1$ , where Fickian transport is recovered in the limit  $\gamma = 1$ . The deviations from Fickian behavior are pronounced at low temperatures and in formulas that have the larger anion.

The work reviewed in this chapter is not yet complete. The analysis of simulation outcomes for the Tf formula is preliminary, and as shown in Figure 5.7a, the model is systematically shifted to shorter timescales than the experiment. More importantly, the discussion of diffusion rate was based on  $\tau$  alone, which neglects the coupling between  $\tau$  and  $\gamma$ . This will be corrected by calculating the mean-squared displacements as a function of time for each optimized set of  $\gamma$  and  $\tau$ , as discussed elsewhere [80,81].

Finally, we note that other phenomena in CA deprotection kinetics could present as anomalous diffusion, such as non-isothermal effects due to the exothermic heat of reaction. Studies are underway to address this point and are discussed in the final chapter of this thesis. However, the preliminary outcomes discussed in this chapter are consistent with studies of anomalous transport in inert glassy polymers, and the scaling with temperature, acid-anion size, and plasticizer concentration demonstrate that dynamical properties of the polymer are at least partly controlling deprotection kinetics in these systems.

## Chapter 6 Characterizing acid diffusion lengths

Chemically amplified resists are essential for high-throughput projection lithography. The intrinsic resolution of these materials is limited by the diffusion length of acid catalyst in the polymer resin. As feature sizes approach 10 nm, there is significant demand for models that predict spatial extent-of-reaction with nanoscale resolution. It is difficult to construct and validate lithography models because there are few experimental techniques that can visualize acid transport in a reacting photoresist [114]. Instead, several indirect methods have been developed to predict acid diffusion rates at industrially relevant temperatures (i.e., below the photoresist's glass transition). These techniques detect a "signal" that is controlled by diffusion, such as deprotection kinetics [9, 72] or the bulk ionic conductivity [65]. However, when extracting acid diffusivities from indirect measurements, the outcome will depend on the type of transport model that is selected for data analysis.

A common indirect approach to evaluate acid diffusion is based on a bilayer experiment, where an acid "feeder layer" is placed in contact with a photoresist film. When the bilayer is heated, the acid can diffuse from the feeder layer into the photoresist and catalyze the deprotection reaction. The average extent-of-deprotection is measured with infrared absorbance spectroscopy as a function of time, and these data are employed to determine appropriate parameters for models or simulations that describe the coupled reaction-diffusion process at the macroscopic [9, 71] or mesoscopic [72] level. For glassy ESCAP [115] and APEX [115] photoresists, the best-fit model parameters predict acid diffusivities on the order of  $10^{-14}$  cm<sup>2</sup>/sec and  $10^{-16}$  cm<sup>2</sup>/sec in protected [9, 71, 72, 74] and deprotected [72, 116] resins, respectively, assuming an underlying Fickian transport process. A related approach employs a trilayer sample, where a film of inert deprotected photoresist is sandwiched between an acid feeder layer and a reactive detector layer. When the system is heated, the acid diffuses through the deprotected photoresist to the detector and catalyzes a reaction that is monitored with time-resolved infrared absorbance spectroscopy. Therefore, the acid arrival time in the detector layer is controlled by acid diffusivity and the photoresist layer thickness. The trilayer platform has not been applied at industrially relevant temperatures because acid diffusivities in deprotected photoresist are very low, and with the typical experimental time scales and film thicknesses, the acid arrival time might be too long to be detected [4]. It is also possible that acid catalyst is trapped by secondary interactions with the polar deprotected polymer [9]. However, when the deprotected photoresist is heated above it's glass transition temperature, then acid arrival is detected and the estimated diffusivities are on the order of  $10^{-12}$  cm<sup>2</sup>/sec [73]. Much like the bilayers, the data are analyzed with the assumption of Fickian transport.

The measured acid diffusion rates in ESCAP and APEX photoresists are extremely low, so it is likely that acid transport will control the deprotection kinetics. However, measured deprotection rates cannot be described with a fast firstorder deprotection reaction coupled to slow Fickian transport of acid catalyst, because the observed deprotection rates are too fast at short times, [73, 80, 116, 117] too slow at long times, [73, 80, 90, 116] and exhibit a nonlinear dependence on acid concentration [80, 109]. It is possible that reaction kinetics are strongly influenced by the dynamics of a glassy polymer matrix. For example, several studies suggest that acid diffusivities and deprotection rates are reduced in ultrathin photoresist films, [64, 118, 119] which is consistent with suppressed polymer dynamics due to confinement [86]. Therefore, while Fickian transport models are commonly applied, their use might not be justified for these complex materials.

In a recent study, we suggested that acid transport in glassy photoresists can

present with anomalous (non-Fickian) character. We measured bulk deprotection rates in a glassy polymer resin (single layer) using time-resolved infrared absorbance spectroscopy, and we interpreted these data with spatially resolved stochastic simulations, where deprotection kinetics was modeled with subdiffusive acid transport coupled to a phenomenological second-order acid loss [80]. This simple approach captured experimental data at all time scales and acid concentrations, and the outcomes were consistent with the extremely slow diffusion rates predicted from bilayer and trilayer experiments. Anomalous transport is common in many classes of condensed soft matter, including examples of probe diffusion in inert polymer glasses, and such behavior is often attributed to spatial heterogeneities in dynamics [82,83]. The origin of the second-order acid loss remains unclear, but this mechanism is able to describe a broad range of data, so it is most likely associated with the underlying chemistry of these systems. In fact, a recent study of deprotection kinetics in a 193 nm photoresist (2-methyl 2-adamantyl protecting groups) reported a competing reaction pathway (dimerization of by-products) that is responsible for acid loss [110].

The aims of the present work are (i) to examine the role of polymer dynamics on the anomalous character, and (ii) test the predictive capability of our simple model through patterning experiments. To assess the role of polymer dynamics, we introduced an inert plasticizer to increase free volume in the polymer and alter matrix dynamics [81]. We anticipated a reduction in the anomalous diffusion behavior, a hypothesis first confirmed with the data presented herein. To evaluate the predictive capability of this model for lithography, we simulated latent image formation using the bulk transport parameters, and then compared these trends with measured line widths in nanopatterned films. The simulated patterning behavior is consistent with experiments, suggesting that this model has potential to predict resolution limits in chemically amplified resists.



Figure 6.1: Simulation algorithm illustrated in two-dimensions for clarity.

## 6.1 Procedures

### 6.1.1 Materials

The chemically amplified resists were prepared from the following components: The polymer resin was poly(4-hydroxystyrene-co-*tert* butyl acrylate) (PHOST-PTBA), 60% HOST, supplied by DuPont Electronic Materials. The photoacid generator was triphenyl sulfonium perfluoro-1-butanesulfonate (PFBS) purchased from Sigma Aldrich. Some resist formulas also contained the inert plasticizer dioctyl phthalate (DOP). The PHOST-PTBA, PFBS, and DOP were dissolved in propylene glycol monomethyl ether acetate (PGMEA) at the desired concentrations, which are reported relative to the solvent. Typical concentrations for PHOST-PTBA and DOP were 10 wt%. All experiments used PFBS concentrations of 1, 2, and 4 wt%. Substrates were double-side polished p-type silicon wafers (standard resistivity), and were cleaned with Piranha solution prior to use. The glass transition temperature of PHOST-PTBA was measured with spectroscopic ellipsometry, and is approximately 140 °C irrespective of the PFBS or DOP loading. A similar invariance of glass transition temperature with additive loading has been observed in other studies [120]. The glass transition temperature of the deprotected polymer is approximately 160 °C.

#### 6.1.2 Deprotection experiments

The resists were cast into films that were approximately 300 nm thick, and then the films were baked at 130 °C for 2 min to remove residual solvent. The acid catalyst was fully activated (throughout the depth of the film) by exposing the films to deep ultraviolet light (254 nm) at a dose of 135 mJ/cm<sup>2</sup>. Each film was post-exposure baked (PEB) at fixed temperature (either 70, 80, or 90 °C) for a specified duration of time, then the changes in chemistry were measured with Brewster angle Fourier-transform infrared (FTIR) spectroscopy. The absorbance at 1149 cm<sup>-1</sup>, corresponding with the C-O-C stretch of PTBA, was measured for each sample. The absorbance data are used to calculate deprotection level as a function of time, where deprotection level is defined as the fraction of TBA groups that were cleaved through the acid-catalyzed deprotection reaction [80]. Each data set is comprised of three PFBS concentrations at constant PEB temperature and fixed DOP loading. To analyze each data set (next paragraph), the deprotection profiles for all PFBS concentrations were collapsed onto a master curve by re-scaling the time axis according to  $t \times [PFBS]^n$ , [80] where *n* ranges from 1.3 to 1.6.

#### 6.1.3 Analysis of deprotection experiments

Following the methods reported elsewhere, [80] simulations of reaction coupled to non-Fickian acid diffusion were implemented on a three-dimensional lattice (1 nm<sup>3</sup>/cell). Acid was uniformly distributed throughout the simulation volume at concentration levels that correspond with experimental conditions. Acid translations were modeled with a non-ergodic, non-Markovian waiting time distribution with longtail kinetics that reproduces subdiffusive behavior [80, 121]. A key attribute of this effort is the ability to describe the diffusion process with only two parameters, a timescale  $\tau$  and an anomalous exponent  $\gamma < 1$ , whose values are determined through comparison with experimental data. The local deprotection reaction was assumed to be instantaneous, because many studies have shown that acid diffusion is the overall controlling step in these systems [9, 71-74]. An acid annihilation mechanism is needed to fit the experimental data at long times. This acid loss mechanism follows second-order kinetics, and is implemented following a simple rule where two acids in the same cell combine to form one unit (see Figure 6.1). The simulations were fit to each experimental data set (master curve) using a simulated annealing algorithm with the adjustable parameters  $\tau$  and  $\gamma$ . Fifty runs were performed for each data set, and within each run, 200 simulations were performed to evaluate residuals and guide the optimization process. This feature of the analysis underlines the need for numeric models that are rapidly evaluated to assess the relevant parameters. The best-fit values of  $\gamma$  and  $\tau$  can describe all acid loadings and are only a function of PEB temperature and DOP loading (i.e., the same parameters can describe all acid concentrations). The optimization algorithm employed  $30 \times 30 \times 30$  cells, while final simulated deprotection profiles in Figure 6.3 were generated with  $50 \times 50 \times 50$  cells. Error bars represent  $\pm 1$  standard deviation. It is important to emphasize that more complex mathematical schemes with additional parameters are straightforward to implement, but our data suggest that the previously described methods are sufficient to capture the observed behavior at industrially relevant length and time scales. Furthermore, noise in the experimental data hinders reliable application of more complex models with additional parameters.

#### 6.1.4 Nanopatterning

Resist films (330-370 nm thick) containing 4 wt% PFBS, with and without 10 wt% DOP, were patterned with single-pass lines using electron beam lithography. The beam voltage and current were 50 kV and 100 pA, respectively, and a 5 nm shot pitch was employed. The dose was varied from 450 to 800  $\mu$ C/cm<sup>2</sup> in increments of 50  $\mu$ C/cm<sup>2</sup>. The pattern layout was designed to minimize proximity effects: Each patterned region was comprised of 20 lines that were 3  $\mu$ m long on a 1.5  $\mu$ m pitch. Adjacent regions were separated by 15  $\mu$ m of empty space (along x or y axes). The conditions for PEB were 90 °C and 30 sec. Patterns were developed in 0.1 N tetramethylammonium hydroxide for 30 sec, then rinsed in de-ionized water and dried under nitrogen flow. Patterns were sputter-coated with approximately 4 nm of tungsten and imaged with a scanning electron microscope (SEM) under the following conditions: accelerating voltage 15 kV, working distance of 5 mm, and magnifications in the range of 150k to 250k. Average line widths were calculated from at least three images per dose using an edge-detection routine implemented in Matlab<sup>®</sup>. Error bars represent ±1 standard deviation.

#### 6.1.5 Simulations of nanopattern formation

Simulations of nanopattern formation were implemented on a three-dimensional lattice of  $100 \times 100 \times 100$  cells (1 nm<sup>3</sup>/cell). The initial spatial distribution of PFBS catalyst (illustrated in Figure 6.2) was selected from a Gaussian probability function and introduced at the center of the simulation system. The full-width at halfmaximum was fixed at 19 nm, which was calculated by assuming a 4 nm diameter electron beam (per instrument manufacturer) broadened by 15 nm of forward scattering (330 nm thick resist at 50 kV) [122, 123]. We did not include proximity effects due to low-angle backscattering because the line patterns in experiments were sparse. The number of acid particles assigned to the lattice was determined by the average PFBS concentration in experiments (4 wt%, or 0.05/nm<sup>3</sup>). The reaction-diffusion model was implemented as described in Section 6.1.3. The total reaction time was set at 30 sec, and the transport parameters  $\tau$  and  $\gamma$  were fixed based on the best-fit



Figure 6.2: Initial spatial distribution of PFBS catalyst for nanopatterning simulations.

results from analysis of bulk deprotection data at 90 °C.

## 6.2 Results and discussion

The experimental and simulated deprotection levels for glassy resists without DOP are compared in Figure 6.3a-c for PEB conditions of 70 °C, 80 °C, and 90 °C. Each PEB condition includes three PFBS loadings of 1 wt%, 2 wt%, and 4 wt%. In all cases, the deprotection rate quickly rises at short-to-intermediate PEB times, but decelerates at long times. Similar behavior is observed in experiments by other research groups, and as discussed in our prior work, these features are not provided by Fickian diffusion coupled to first-order deprotection and/or first-order acid trapping reactions [80]. Fickian diffusion always under-estimates the deprotection level at short times, and first-order acid trapping cannot describe the long-time behavior for all PFBS concentrations. However, the anomalous transport model with acid-acid annihilation offers near-quantitative agreement with experimental data, although some deviations persist at very long PEB times (ca. > 2 hours). The deviations at long



Figure 6.3: Experimental deprotection levels (symbols) and best-fit simulations (lines) for 1 wt%, 2 wt%, and 4 wt% acid loading. a) 70 °C, b) 80 °C, c) 90 °C, and d) 90 °C with 10 wt% DOP.

times may result from slow environmental contamination that deactivates the acid catalyst, or perhaps a gradual densification of the film that reduces the rates of acid transport. In any case, the long time limit is not relevant for industrial applications. Most importantly, the model captures kinetics for all PFBS concentrations, so outcomes can then be scaled to higher PFBS loadings that are representative of industrial formulations.

The effect of PEB temperature on best-fit model parameters  $(\tau, \gamma)$  is summarized in Figure 6.4a-b. (These values are slightly different than reported in our previous work that included experimental data up to 10 wt% PFBS loading [80]. We no longer consider high PAG loadings because the deprotection rates are too fast for reliable measurement with our ex-situ FTIR protocol.) First, we note that increasing the PEB temperature produces a corresponding increase in deprotection rate. This behavior is summarized in Figure 6.4a, which reports the diffusion-controlled reaction rate  $(1/\tau)$  as a function of inverse temperature (1/T). The scaling is consistent with Arrhenius kinetics, although more data points are required to distinguish between Arrhenius kinetics and the Williams-Landel-Ferry model that is common for glassy polymers [109, 116]. Second, we find that  $\gamma$  increases with PEB temperature, meaning the model approaches Fickian character at higher temperatures (note that  $\gamma \rightarrow 1$  reproduces Fickian transport). This behavior is reported in Figure 6.4b. The values of  $\gamma$  fall in the range of 0.6 to 0.8, which is consistent with studies of isothermal probe diffusion in inert polymer glasses [83, 112].

The observed anomalous kinetics could be associated with transient free volume generation, [73, 124] plasticization from volatile reaction by-products, [73, 124] nonisothermal effects, [116] and coupling between acid transport and local heterogeneities in polymer dynamics. [80] Transient free volume and by-product plasticization were rigorously examined for poly(*tert*butoxycarbonyl-oxystyrene) resins, and these studies determined that neither factor is controlling the reaction kinetics [125]. Nonisothermal effects may be relevant, as the exothermic heat of reaction could increase the temperature within the film and enhance the diffusion rate. Further studies are underway to examine this hypothesis. In the present study, we considered the effects of polymer dynamics on reaction kinetics. We incorporated the plasticizer DOP to increase free volume in the polymer film, and the impact on deprotection rates is seen by comparing Figure 6.3c and Figure 6.3d. While these experiments were performed with the same PEB temperature, the deprotection rates are visibly enhanced by DOP, suggesting that the acid-counterion pair can diffuse more rapidly throughout



Figure 6.4: a) Deprotection rate  $1/\tau$  as a function of temperature; b) Anomalous exponent  $\gamma$  as a function of temperature. Note that  $\gamma < 1$  reproduces subdiffusive transport, while  $\gamma = 1$  represents Fickian transport.

the plasticized polymer film. The best-fit values of  $\tau$  and  $\gamma$  for resists with DOP are reported in Figure 6.4a-b: The deprotection rate is approximately 66% faster with DOP, and the anomalous exponent  $\gamma$  is increased from approximately 0.7 to 0.8. The latter point is particularly interesting, because the increase in anomalous exponent points to a shift in the underlying time-dependent diffusion mechanism. One possible explanation for this behavior is a non-isothermal effect, where faster diffusion in the plasticized film leads to increased deprotection rates, and a corresponding increase in heat effect then further accelerates the diffusion. An alternative explanation is that plasticization by DOP increases the average diffusion rate and also reduces the coupling between transport and local heterogeneities. While we cannot definitively identify a sole underlying cause of anomalous kinetics, it is clear that dynamical properties in the polymer resin play an important role in the reaction-diffusion mechanism.

A question that remains is whether the parameters extracted from bulk analysis can predict lithographic properties. We exposed line patterns in each resist formula using electron beam lithography (EBL), and then compared experimental outcomes with simulations of nanopattern formation. For experiments, resists with 4 wt% PFBS (with and without DOP) were patterned by EBL (sparse, single-pass lines). The post-exposure bake was implemented at 90 °C for 30 sec, and then patterns were developed for 30 sec to form a relief image of long trenches (with depths equal to resist thickness). The widths of these line patterns (trenches) were measured with scanning electron microscopy (SEM). Simulations were devised to match electron beam lithography experiments: The reaction-diffusion model was implemented with the best-fit values of  $\gamma$  and  $\tau$  for each resist formula at 90°C, which are summarized in Figure 6.4. The initial spatial distribution of acid was based on an average 4 wt% acid loading and incorporated the forward electron scattering through a 330 nm thick resist film. The simulated reaction time was 30 sec.

Representative SEM images of developed line patterns are reported in Figure 6.5a). Measured line widths are summarized in Figure 6.5b) as a function of DOP loading and electron beam dose, where each data set (symbols connected by lines) reflects the outcomes of an individual patterning experiment. There is scatter among data sets, but it is clear that adding DOP will increase the line width (by a factor of 1.5 to 3). This is qualitatively consistent with analysis of bulk experiments, as we observed increased deprotection levels with the addition of DOP (0.68 compared with 0.48 after 30 sec at 90°C). A higher deprotection level can enhance the dissolution kinetics. However, we note that resist solubility differs for formulas with and without



Figure 6.5: a) Line width for each resist formula as a function of exposure dose. b) Examples of SEM measurements for each formula, exposure dose of 600  $\mu$ C/cm<sup>2</sup>. c) Normalized residual thickness (NRT) for each resist formula as a function of deprotection level (30 sec development).

DOP, and this also controls the dissolution kinetics and ultimate line widths. Resist solubility was evaluated by immersing bulk films with varying deprotection levels in the developer for 30 sec. The thickness of the film was measured before  $(t_i)$  and after  $(t_f)$  development. Figure 6.4c) reports the normalized residual thickness (NRT =  $t_f/t_i$ ) as a function of average deprotection level. These data demonstrate that DOP, a non-polar additive, inhibits dissolution in the polar developer, but the solubility switch is effected at low deprotection levels in both formulas. These observations underline the need to couple simulations of pattern formation with models for dissolution that reflect the resist composition. The image maps in Figure 6.6a) show simulated deprotection profiles averaged along the z-axis (through the film thickness). The color scale illustrates the transition from no deprotected sites (blue) to a maximum deprotection level of 0.7 (red), and the solid black contour marks an average deprotection level of 0.33. The line profiles in Figure 6.6b) report the initial acid distribution and final deprotection levels averaged along both z and x axes. The simulations predict image blur due to acid diffusion in both formulas, but this effect is more pronounced for resists that include DOP. The simulations also predict that DOP will generate a higher level of deprotection near the center of the line.

The measured line widths are larger than predicted by simulations, but there are several reasons why quantitative agreement is not anticipated at this stage. First, the simulations do not account for proximity effects due to electron backscatter in EBL. Considering the sparse pattern layout in experiments, we do not anticipate a large proximity effect. However, the data in Figure 6.5c) demonstrate that very low deprotection levels can effect the solubility switch, so even a small amount of activation due to low-angle backscattering could impact the tails of the latent images. Second, the resist/developer system offers very poor lithographic contrast, and is therefore not a great model for patterning experiments (as evidenced by the large



Figure 6.6: a) Image maps of simulated deprotection level (averaged through film thickness) for 30 sec PEB at 90°C. b) Deprotected line width at 30 sec and initial spatial density of acid catalyst.

variance in measured line widths). Third, and most importantly, the simulations do not include a model for resist dissolution. Experiments demonstrate that DOP reduces the solubility of the polymer in the developer (Figure 6.5c), so one might expect slower dissolution at the "tails" of the latent image (where deprotection levels are low). However, the model predicts that DOP will increase the deprotection level and reduce heterogeneity in composition (Figure 6.6), and these factors might enhance dissolution rates near the center of the line.

## 6.3 Conclusions

The acid-catalyzed deprotection of glassy photoresists was measured with Fouriertransform infrared spectroscopy as a function of PEB time, acid loading, and PEB temperature. Data were interpreted with a simple and accurate model based on subdiffusive acid transport coupled to a second-order acid loss. The model can describe experimental data that span a wide range of time scales and acid concentrations, with only two temperature-dependent fitting parameters: A characteristic time scale for acid translations ( $\tau$ ), and an anomalous exponent ( $\gamma$ ) that reflects the deviations from Fickian transport (specifically, the underlying non-Gaussian distribution of acid hopping times). We demonstrated that anomalous kinetics are influenced by the dynamical properties of the polymer resin, which was verified by adding plasticizing agents to the resist, and we discussed other factors that might be relevant (such an non-isothermal effects). Finally, we presented patterning data where the measured line widths were in qualitative agreement with simulated latent images. We conclude that lithographic resolution might be predicted from simple FTIR measurements coupled to spatially resolved simulations. Future experiments will evaluate bulk deprotection rates and nanopattern formation in resist with higher contrast, and simulations will be adapted to incorporate models for resist dissolution.

# Chapter 7 Outlook

Trilayer experiments were performed to gain more insight into the anomalous diffusion mechanism. Trilayer refers to three polymer layers stacked on top of each other where each layer has its own role. Two layers of polymers were first used to study motion of polymeric chain between polymer melts ( $T \gg T_g$ ) Karim1990, Stamm1991, Karim1994. Bilayers of isotopically labeled polymers have been investigated by neutron reflectometry and conclusions have been drawn about nature of diffusion in time and temperature range studied. More recent bilayer studies involve work of Lin et al, who used bilayer technique coupled with neutron reflectivity measurements to assess the effect of polymer-substrate interaction energy on the interdiffusion between isotopically labeled ultrathin (3-30 nm) films of PMMA [126]. Torkelson and co-workers studied diffusion of inert dye molecule from one layer to another in a bilayer using non-radioactive energy transfer [84]. Use of bilayers to model diffusion in CAR has been discussed in detail in previous chapter.

Postnikov et al [73] first used a trilayer approach to model the diffusion in CAR. As shown in Figure 7.1, a top layer in the stack is an acid reservoir layer. An intermediate layer is sandwiched between top acid layer and the detector layer at the bottom. Detector layer serves to detect the onset of the acid from acid layer as it diffuses through the intermediate layer. The order of feeder and detector layer can be reversed. The thickness of the intermediate layer decides the distance required by acid catalyst to travel before it reaches the detector layer. Acid arrival is detected by reduction in absorbance of the acid labile protecting group in *in situ* IR.

Feeder	0	• •	•••	•••	0 8	S	٢	000	• •	۲
Interme	diate	9								
Detector	-									
Si										

Figure 7.1: A sample trilayer geometry. Top (feeder) layer is loaded with photoacid generator.

#### 7.0.1 Objective of trilayer experiments

Among all intermediate polymer layers studied, Postnikov et al did not detect any diffusion of acid across the intermediate layer of PHOST. PHOST film thicknesses were 135 and 600 nm and PEB temperatures were 70°C and 100°C respectively. (PHOST  $T_g = 165^{\circ}$ C) [127] Stewart et al carried out similar trilayer experiments and were not able to detect diffusion across 500-1100 nm thick films of PHOST at PEB temperature as high as 160°C [4].

We believe that the film thicknesses used in these experiments were so high, the acid catalyst could not diffuse across the intermediate layer even though the experiments were carried out for prolonged times. For example, using a typical diffusion coefficient  $1 \times 10^{-16}$  cm<sup>2</sup>/sec reported by Wallraff et al [12], it will take about 10 days for an acid catalyst to diffuse through 135 nm film of PHOST at PEB temperature of 85°C. We do not report very high mean square displacement values using our model at temperatures used by Postnikov and co-workers. For PFBS as PAG and PEB of 30 sec at 90°C, our model predicts an MSD value of 24 nm<sup>2</sup> or diffusion length of ~5 nm [81]. We believe diffusion can be detected by reducing the intermediate film thickness while using industrially relevant PEB temperatures. Trilayer experiments are also a great way of decoupling reaction and diffusion. In a single layer

of CAR, reaction and diffusion are coupled processes. In trilayer experiments, only diffusion occurs in intermediate layer leaving out local reaction related phenomena like non-isothermal effects.

The objectives of these experiments are to a) verify detection of diffusion across intermediate layer using reasonable thicknesses and relevant temperatures b) calculate the diffusion times for films of various thicknesses (diffusion lengths) and compare it with the predictions from our model.

#### 7.0.2 Construction of trilayer

Bilayers that were used before were constructed by floating method. A first layer of polymer film is spin-coated on the substrate (usually silicon wafer). The second film is prepared on a microscopic slide by spin-coating as well. A razor blade is then used to cut a film in the center of the slide of the desired size. The slide is immersed in a pool of de-ionized water releasing the film. This floating film is then captured carefully on top of polymer film that was spin-coated on substrate forming a bilayer specimen. For construction of trilayer, Postnikov et al [127] spin coated first two layers (feeder and intermediate layer) on top of each other. Care was taken to use orthogonal solvents - solvent of second layer will not dissolve first layer. The top layer, detector layer, was prepared by floating method mentioned above.

For our trilayer system, we used 5 wt% polymethoxystyrene (PMOS) in PGMEA for feeder layer. Photoacid generator (PFBS) was added to this solution. After spincoating PMOS + PAG on Piranha-cleaned Si wafer at 3000 rpm and post-apply bake (PAB) of 2 mins at 130°C gives a 100-110 nm film. Feeder layer thickness does not play a significant role since it only acts as acid reservoir. However,  $T_g$  of the feeder layer is important in the sense that it has to be lower than  $T_g$  of the intermediate PHOST layer so that feeder layer is mobile enough at experimental temperature that



Figure 7.2: Optical microscopy images of spin-coated PHOST layer on PMOS+PAG layer. (a) shows a conformal bilayer with 1-butanol as solvent for PHOST (b) shows a non-conformal film when anhydrous ethanol was used as a solvent for PHOST.

it releases the acid.  $T_g$  of PMOS is 91°C and  $T_g$  of PHOST is 160°C [128]. For intermediate layer, we used two solvents - anhydrous ethanol and 1-butanol. It was confirmed beforehand that neither of these solvents dissolve PMOS. Figure 7.2 shows optical microscopy images of a PHOST layer spin-coated on top of PMOS + PAG layer using both solvents. It is clear from the optical microscopy images that we get conformal film only using 1-butanol as solvent. This was also verified by measuring thicknesses at each step using spectroscopic ellipsometry. Bilayer, with 1-butanol as solvent for PHOST, gives an expected increase in thickness after spin-coating PHOST as second layer.

## The third layer

After bilayer scheme was perfected, the options to prepare a third film were floating, spin-coating, or stamping the film from a poly(dimethylsiloxane) (PDMS), a technique used by Kang and co-workers to study diffusion in CAR [9]. Stamping approach involves preparing a slab of PDMS, treating it in a ultra violet ozone cleaning



Figure 7.3: Optical microscopy image of a PtBA film stamped on top of a PMOS layer using PDMS samping method. (a) shows a hole left behind due to uneven release of the film from PDMS slab (b) zoomed in version of (a) shows wavy nature of the film.

system (UVOCS) to make it hydrophilic, spin-coat detector layer on it, and then directly and gently stamp it on top of bilayer and gradually withdraw PDMS which will leave the detector layer on top of bilayer. After several trials of varying the PDMS slab contact angle, and detector layer polymer used, we discontinued stamping approach because (a) the stamped layer had holes in few places (b) stamped film was wavy which was due to the wavy surface of PDMS slab. Figure 7.3 shows sample image of a detector layer film stamped directly on top of a feeder layer PMOS film.

Spin-coating a third layer on top of existing bilayer would require coming up with a solvent that will dissolve detector layer and will not dissolve PMOS and PHOST. Detector layer candidates were PS-PtBA and PtBA. We could not find a suitable solvent to meet this criterion.

As our third option, we made several attempts to float a suitable detector layer off of a glass slide. These films did not float well off of a glass slide. A 30 nm watersoluble polyethylenedioxythophene polystyrenesulfonate (PEDOT:PSS) film had to be coated first on the slide before spin-coating detector layer to facilitate release of

Layer	Polymer	Solvent	Method of applying	Thickness (nm)
Feeder	PMOS + PAG	PGMEA	Spin-coating	100-110
Intermediate	PHOST	1-butanol	Spin-coating	Variable
Detector	PtBA	PGMEA	Floating	300-330

Table 7.1: Working trilayer scheme.



Figure 7.4: Optical microscopy image of a 2 in  $\times$ 2 in trilayer. (a) Area of the trilayer shows some cracking of the detector layer. (b) Area from the same trilayer that is uniform. A 250  $\mu$ m circle in the middle shows approx. area of the IR beam.

detector layer in DI water. A finalized working trilayer is described in Table 7.1.

The film captured with floating method is not uniform throughout and care has to be taken that IR beam passes through a region that is verified for its uniformity under optical microscopy. Approximate diameter of the IR beam used for our experiments is 250  $\mu$ m. This has been demonstrated in Figure 7.4.

#### Heat cell for *in situ* experiments

IR absorbance is measured with the same Nicolet NEXUS 6700 FTIR spectrometer equipped with a Brewster angle sample stage that was used for bulk deprotection experiments. We devised a simple heating stage to carry out trilayer experiments *in* 



Figure 7.5: FTIR heat cell for trilayer experiments.

situ which allows to collect many IR spectra during the experiment from the same sample. This heat cell can be seen in Figure 7.5. Its made up of two blocks of aluminium, with half inch diameter through holes in center, that will clamp the wafer with trilayer on it. A heating element next to the wafer will heat the block and temperature controller controls the temperature with feedback from a thermocouple. The stage is kept at an angle 16° (Si Brewster angle) same as before. It takes a min for the heat cell to reach 60°C and total of 3 mins to reach 90°C. IR chamber is purged with constant N<sub>2</sub> gas flow during the experiment.

### **Preliminary results**

To test if we detect any diffusion through an intermediate PHOST, we prepared a trilayer as per description in previous sections. We did not use heat cell for this experiment. Feeder layer contained 4 wt% Tf and gave a film of approx. 115 nm. After PAB, 0.125 wt% PHOST was spin-coated from 1-butanol. This concentration gives a 4 nm film. Finally, trilayer was completed by floating and capturing a 10



Figure 7.6: A trilayer diffusion experiment showing reduction in IR absorbance of tBA group at 1150 cm<sup>-1</sup> implying diffusion of acid catalyst across 4 nm PHOST film into the detector layer. Heat cell was not used for this experiment.

wt% PtBA film. Total stack thickness was 415 nm. After UV exposure, the stack was post exposure baked at 90°C for 15 mins, a sufficiently long enough time. The result of this experiment is shown in Figure 7.6. We observe a clear reduction in IR peak corresponding to tBA moiety. This implies the acid catalyst has diffused across PHOST film into detector layer. Initial objective of this project, devise a trilayer and verify if there is diffusion across an ultrathin PHOST film, has been completed. This experiment does not tell us the time required to diffuse through the intermediate layer. An *in situ* diffusion experiment using heat cell where multiple spectra can be taken during the duration of experiment and exact moment when absorbance starts going down (acid arrival) can be found out is required. This is shown in Figure 7.7.



Figure 7.7: In situ trilayer diffusion experiment showing IR absorbance vs. time. The drop in absorbance is indicative of onset of acid in detector layer.  $t_{diff}$  is time required for diffusion through intermediate layer [4].

## References

- [1] D. E. Hudgin, ed., Fundamentals of polymer engineering. McGraw-Hill, 1997.
- [2] O. A. G. K. van der Wel, "Moisture transport and equilibrum in organic coatings," *Heron*, vol. 45(2), pp. 125–152, 2000.
- [3] M. Ediger, "Spatially heterogeneous dynamics in supercooled liquids," Annual review of physical chemistry, vol. 51, pp. 99–128, 2000.
- [4] M. D. Stewart, Catalyst diffusion in positive-tone chemically amplified photoresists. PhD thesis, 2003. Copyright - Copyright UMI - Dissertations Publishing 2003; Last updated - 2014-01-08; First page - n/a; M3: Ph.D.
- [5] C. T. Moynihan, N. Balitactac, L. Boone, and T. A. Litovitz, "Comparison of shear and conductivity relaxation times for concentrated lithium chloride solutions," *The Journal of Chemical Physics*, vol. 55, no. 6, pp. 3013–3019, 1971.
- [6] S. C. Kuebler, D. J. Schaefer, C. Boeffel, U. Pawelzik, and H. W. Spiess, "2d exchange nmr investigation of the alpha-relaxation in poly(ethyl methacrylate) as compared to poly(methyl methacrylate)," *Macromolecules*, vol. 30, no. 21, pp. 6597–6609, 1997.
- [7] D. Schaefer and H. W. Spiess, "Two dimensional exchange nuclear magnetic resonance of powder samples. iv. distribution of correlation times and line shapes in the intermediate dynamic range," *The Journal of Chemical Physics*, vol. 97, no. 11, pp. 7944–7954, 1992.

- [8] K. Fukao, "Dynamics in thin polymer films by dielectric spectroscopy," Eur. Phys. J. E, vol. 12, no. 1, pp. 119–125, 2003.
- [9] S. Kang, W.-l. Wu, K.-W. Choi, A. De Silva, C. K. Ober, and V. M. Prabhu, "Characterization of the photoacid diffusion length and reaction kinetics in euv photoresists with ir spectroscopy," *Macromolecules*, vol. 43, no. 9, pp. 4275– 4286, 2010.
- [10] P. B. Meggs, A history of graphic design. New York : John Wiley & Sons, 1998.
- [11] D. Kauzlarick, ed., Fundamentals of microfabrication, the science of miniaturization. IEEE Engineering in Medicine and Biology Magazine, 2003.
- [12] G. M. Wallraff, W. D. Hinsberg, F. A. Houle, M. Morrison, C. E. Larson, M. Sanchez, J. Hoffnagle, P. J. Brock, and G. Breyta, "Experimental method for quantifying acid diffusion in chemically amplified resists," in *Microlithography* 1999: Advances in Resist Technology and Processing XVI, Pts 1 And 2 (Conley, W., ed.), vol. 3678 of Proceedings of the Society of Photo-optical Instrumentation Engineers (SPIE), pp. 138–148, 1999. Microlithography 1999, Santa Clara, CA, MAR 15-17, 1999.
- [13] J. K. C. Chiang, Design for manufacturability and yield for nanoscale cmos. Springer, 2007.
- [14] M. Rothschild, "Projection optical lithography," *Materials today*, vol. 8, pp. 18–24, FEB 2005.
- [15] T. Ito and S. Okazaki, "Pushing the limits of lithography," Nature, vol. 406, pp. 1027–1031, AUG 31 2000.

- [16] G. Willson, R. Miller, D. McKean, N. Clecak, T. Tompkins, D. Hofer, J. Michl, and J. Downing, "Design of a positive resist for projection lithography in the mid-uv," *Polymer Engineering & Science*, vol. 23, no. 18, pp. 1004–1011, 1983.
- [17] C. Willson, R. D. Miller, D. R. McKean, and L. A. Pederson, "New diazoketone dissolution inhibitors for deep u.v. photolithography," *Proc. SPIE*, vol. 0771, pp. 2–10, 1987.
- [18] K. Jain, C. Willson, and B. Lin, "Ultrafast deep uv lithography with excimer lasers," *Electron Device Letters*, *IEEE*, vol. 3, pp. 53–55, Mar 1982.
- [19] K. Jain, S. Rice, and B. J. Lin, "Ultrafast deep uv lithography using excimer lasers," *Polymer Engineering & Science*, vol. 23, no. 18, pp. 1019–1021, 1983.
- B. Lin, B., "Deep uv lithography," Journal of vacuum science and technology, vol. 12, no. 6, pp. 1317–1320, 1975.
- [21] T. Iwayanagi, T. Kohashi, S. Nonogaki, T. Matsuzawa, K. Douta, and H. Yanazawa, "Azide-phenolic resin photoresists for deep uv lithography," *Electron Devices*, *IEEE Transactions on*, vol. 28, pp. 1306–1310, Nov 1981.
- [22] H. Ito, C. G. Willson, and J. H. Frechet, "New uv resists with negative or positive tone," in VLSI Technology, 1982. Digest of Technical Papers. Symposium on, pp. 86–87, Sept 1982.
- [23] C. G. W. Hiroshi Ito, Polymers in Electronics. American Chemical Society, 1984.
- [24] H. Ito, C. G. Willson, J. M. J. Frechet, M. J. Farrall, and E. Eichler, "Synthesis of poly(p-hydroxy-alpha-methylstyrene) by cationic polymerization and chemical modification," *Macromolecules*, vol. 16, no. 4, pp. 510–517, 1983.

- [25] H. Ito, C. Willson, and J. Frechet, "Positive- and negative-working resist compositions with acid generating photoinitiator and polymer with acid labile groups pendant from polymer backbone," Jan. 1 1985. US Patent 4,491,628.
- [26] J. G. Maltabes, S. J. Holmes, J. R. Morrow, R. L. Barr, M. C. Hakey, G. Reynolds, W. R. Brunsvold, C. G. Willson, N. J. Clecak, S. A. MacDonald, and H. Ito, "1x deep-uv lithography with chemical amplification for 1-micron dram production," *Proc. SPIE*, vol. 1262, pp. 2–7, 1990.
- [27] H. Ito, "Rise of chemical amplification resists from laboratory curiosity to paradigm enabling moore's law," *Proc. SPIE*, vol. 6923, pp. 692302–692302– 15, 2008.
- [28] S. A. MacDonald, N. J. Clecak, H. R. Wendt, C. G. Willson, C. D. Snyder, C. J. Knors, N. B. Deyoe, J. G. Maltabes, J. R. Morrow, A. E. McGuire, and S. J. Holmes, "Airborne chemical contamination of a chemically amplified resist," *Proc. SPIE*, vol. 1466, pp. 2–12, 1991.
- [29] H. Ito, W. P. England, N. J. Clecak, G. Breyta, Ratnam, and W. D. Hinsberg, "Molecular design for stabilization of chemical amplification resist toward airborne contamination," *Proc. SPIE*, vol. 1925, pp. 65–75, 1993.
- [30] D. H. R. S. Hiroshi Ito, Greg Breyta, "Environmentally stable chemical amplification positive resist: principle, chemistry, contamination resistance, and lithographic feasibility," *Journal of Photopolymer Science and Technology*, 1994.
- [31] Y. Kaimoto, K. Nozaki, S. Takechi, and N. Abe, "Alicyclic polymer for arf and krf excimer resist based on chemical amplification," *Proc. SPIE*, vol. 1672, pp. 66–73, 1992.

- [32] R. D. Allen, G. M. Wallraff, R. A. Di Pietro, D. C. Hofer, and R. R. Kunz, "193nm single-layer positive resists: building etch resistance into a high-resolution imaging system," *Proc. SPIE*, vol. 2438, pp. 474–485, 1995.
- [33] I. T. R. for Semiconductors, "Lithography," tech. rep., International Technology Roadmap for Semiconductors, 2013.
- [34] R. A. Lawson, L. M. Tolbert, T. R. Younkin, and C. L. Henderson, "Negativetone molecular resists based on cationic polymerization," Advances In Resist Materials and Processing Technology Xxvi, vol. 7273, p. SPIE, 2009.
- [35] R. Pittman, Morgan & Claypool Life Sciences. 2011.
- [36] J. Siepmann, H. Kranz, R. Bodmeier, and N. Peppas, "Hpmc-matrices for controlled drug delivery: A new model combining diffusion, swelling, and dissolution mechanisms and predicting the release kinetics," *Pharmaceutical Research*, vol. 16, no. 11, pp. 1748–1756, 1999.
- [37] luis m. Vaccarezza and jorge chirife, "On the application of fick's law for the kinetic analysis of air drying of foods," *Journal of Food Science*, vol. 43, no. 1, pp. 236–238, 1978.
- [38] D. Rybski, S. V. Buldyrev, S. Havlin, F. Liljeros, H. A. Makse, and H. E. Stanley, "Scaling laws of human interaction activity," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 106, no. 31, pp. pp. 12640–12645, 2009.
- [39] K. Schaupert, D. Albrecht, P. Armbruster, and R. Spohr, "Permeation through latent nuclear tracks in polymer foils," *Applied Physics A*, vol. 44, no. 4, pp. 347– 352, 1987.

- [40] D. Shaw, ed., Atomic diffusion in semiconductors. Plenum press, 1973.
- [41] F. Höhne G., Hemminger W., Differential Scanning Calorimetry : An Introduction for Practitioners. Springer, 1996.
- [42] M. H. C. D. Turnbull, "Molecular transport in liquids and glasses," *The Journal of Chemical Physics*, vol. 31, p. 1164, 1959.
- [43] J. Vrentas and C. Vrentas, "Predictive methods for self-diffusion and mutual diffusion coefficients in polymer solvent systems," *European Polymer Journal*, vol. 34, no. 5âĂŞ6, pp. 797 – 803, 1998.
- [44] P. Macedo and T. Litovitz, "On the relative roles of free volume and activation energy in viscosity of liquids," *Journal of chemical physics*, vol. 42, no. 1, pp. 245–&, 1965.
- [45] J. Vrentas, James S.; Duda, "Molecular diffusion in polymer solutions," AIChE J, vol. 25(1), pp. 1–24, 1979.
- [46] J. R. P. (ed) Solid State Ionics, vol. 165, p. 1, 2004.
- [47] J. M. Hutchinson and A. J. Kovacs, "A simple phenomenological approach to the thermal behavior of glasses during uniform heating or cooling," *Journal of Polymer Science: Polymer Physics Edition*, vol. 14, no. 9, pp. 1575–1590, 1976.
- [48] J. Kawamura and M. Shimoji Mater. Chem. Phys., vol. 23, p. 99, 1989.
- [49] N. K. O. K. Junichi K, Ryo A, "Ionic transport in glass and polymer : Hierarchical structure and dynamics," *Physics of Solid State Ionics*, vol. 37, pp. 193–245, 2006.

- [50] N. Ramesh and J. Duda, "Diffusion in polymers below the glass transition temperature: Comparison of two approaches based on free volume concepts," Korean Journal of Chemical Engineering, vol. 17, no. 3, pp. 310–317, 2000. cited By 6.
- [51] S. T. M. Odani H, Kida, "Diffusion in glassy polymers. iii. temperature dependence and solvent effects," *Bulletin of the Chemical Society of Japan*, vol. 39(11), pp. 2378–2385, 1966.
- [52] G. Billovits and C. Durning, "Linear viscoeleastic diffusion in the poly(styrene) ethylbenzebe system - differential sorption experiments," *Macromolecules*, vol. 26, pp. 6927–6936, DEC 6 1993.
- [53] H. Odani, J. Hayashi, and M. Tamura, "Diffusion in glassy polymers. ii. effects of polymer-penetrant interaction ; diffusion of ethyl methyl ketone in atactic polystyrene," *Bulletin of the Chemical Society of Japan*, vol. 34, no. 6, pp. 817– 821, 1961.
- [54] A. Kishimoto, H. Fujita, H. Odani, M. Kurata, and M. Tamura, "Successive differential absorptions of vapors by glassy polymers," *The Journal of Physical Chemistry*, vol. 64, no. 5, pp. 594–598, 1960.
- [55] R. Bohmer, K. I. Ngai, C. A. Angell, and D. J. Plazek, "Nonexponential relaxations in strong and fragile glass formers," *Journal of Chemical Physics*, vol. 99, pp. 4201–4209, Sept. 1993.
- [56] U. Tracht, M. Wilhelm, A. Heuer, and H. Spiess, "Combined reduced 4d c-13 exchange and h-1 spin diffusion experiment for determining the length scale of dynamic heterogeneities," *Journal of magnetic resonance*, vol. 140, pp. 460–470, OCT 1999.

- [57] H. Scher and M. Lax, "Continuous time random walk model of hopping transport: Application to impurity conduction," *Journal of Non-Crystalline Solids*, vol. 8åÄŞ10, no. 0, pp. 497 – 504, 1972. Amorphous and Liquid Semiconductors.
- [58] H. Scher and M. Lax, "Stochastic transport in a disordered solid. ii. impurity conduction," *Phys. Rev. B*, vol. 7, pp. 4502–4519, May 1973.
- [59] T. Odagaki and L. M. Mol. Cryst. & Liq. Cryst., vol. 85, p. 1519, 1982.
- [60] J. C. Dyre *Phys.Lett*, vol. 108A, p. 6010, 1985.
- [61] C. E. B. C. B. Briozzo *Phys.Rev.A*, vol. 39, p. 6010, 1989.
- [62] T. Odagaki and Y. Hiwatari, "Stochastic model for the glass transition of simple classical liquids," *Phys. Rev. A*, vol. 41, pp. 929–937, Jan 1990.
- [63] T. Odagaki and Y. Hiwatari, "Gaussian to non-gaussian transition in supercooled fluids," *Phys. Rev. A*, vol. 43, pp. 1103–1106, Jan 1991.
- [64] L. Singh, P. J. Ludovice, and C. L. Henderson, "Effect of nanoscale confinement on the diffusion behavior of photoresist polymer thin films," in Advances in Resist Technology and Processing XXI, Pts 1 And 2 (Sturtevant, J. L., ed.), vol. 5376 of Proceedings of the Society of Photo-optical Instrumentation Engineers (SPIE), pp. 369–378, 2004. Conference on Advances in Resist Technology and Processing XXI, Santa Clara, CA, FEB 23-24, 2004.
- [65] C. H. C. Berger, "Improved chemically amplified photoresist characterization using interdigitated electrode sensors: Photoacid diffusivity measurements," Advances in Resist Technology and Processing XXI, vol. 5376, pp. 392–403, 2004.

- [66] S. H. Kang, V. M. Prabhu, B. D. Vogt, E. K. Lin, W. li Wu, and K. Turnquest, "Effect of copolymer composition on acid-catalyzed deprotection reaction kinetics in model photoresists," *Polymer*, vol. 47, no. 18, pp. 6293 – 6302, 2006.
- [67] H. Watanabe, H. Sumitani, T. Kumada, M. Inoue, K. Marumoto, and Y. Matsui, "Evaluation of acid diffusibility in a chemical amplification resist using water-soluble film," *Jpn. J. Appl. Phys.*, vol. 34, pp. 6780–6785, 1995.
- [68] E. Lin, C. Soles, D. Goldfarb, B. Trinque, S. Burns, R. Jones, J. Lenhart, M. Angelopoulos, C. Wilson, S. Satija, and W. Wu, "Direct measurement of the reaction front in chemically amplified photoresists," *Science*, vol. 297, pp. 372– 375, 2002.
- [69] H. F. Hinsberg WD, "Software architecture for stochastic simulation of nonhomogenous systems," 1998.
- [70] K. Lavery, K. Choi, B. Vogt, V. Prabhu, E. Lin, W. Wu, S. Satija, M. Leeson,
  H. Cao, G. Thompson, H. Deng, and D. S. Fryer, "Fundamentals of rectiondiffusion process in model euv photoresists," *Advances in Resist Technology XXIII, Proc. SPIE*, vol. 6153, pp. 1–7, 2006.
- [71] S. Kang, K. Lavery, K. Choi, V. Parbhu, W. Wu, E. Lin, A. Silva, N. Felix, and C. Ober, "A comparison of the reaction-diffusion kinetics between model-euv polymer and molecular-glass photoresists," *Advances in Resist Materials and Processing Technology XXV, C. L. Henderson, Ed., Proc. SPIE*, vol. 692317, pp. 1–11, 2008.
- [72] G. Wallraff, W. Hinsberg, F. Houle, M. Morrison, C. Larson, M. Sanchez, J. Hoffnagle, P. Brock, and G. Breyta, "Experimental method for quantifying acid diffusion in chemically amplified resists," *Advances in Resist Materials* and Processing Technology XVI, Proc. SPIE, vol. 3678, pp. 138–148, 1999.
- [73] S. Postnikov, M. Stewart, H. Tran, M. Nierode, D. Medeiros, T. Cao, J. Byers, S. Webber, and C. Wilson, "Study of resolution limits due to intrinsic bias in chemically amplified photoresists," *J. Vac. Sci. Technol. B.*, vol. 17(6), pp. 3335–3338, 1999.
- [74] M. Stewart, H. Tran, G. Schmid, T. Stachowiak, D. Becker, and C. Wilson,
  "Acid catalyst mobility in resist resins," J. Vac. Sci. Technol. B, vol. 20(6),
  pp. 2946-2952, 2002.
- [75] I. Hiroshi and W. C. Grant, Applications of Photoinitiators to the Design of Resists for Semiconductor Manufacturing, ch. 3, pp. 11–23.
- [76] W. D. Hinsberg, F. A. Houle, M. I. Sanchez, and G. M. Wallraff, "Chemical and physical aspects of the post-exposure baking process used for positivetone chemically amplified resists," *IBM Journal of Research and Development*, vol. 45, pp. 667–682, SEP 2001.
- [77] G. Wallraff, J. Hutchinson, W. Hinsberg, F. Houle, P. Seidel, R. Johnson, and W. Oldham, "Thermal and acid catalyzed deprotection kinetics in candidate deep ultraviolet resist materials," *Journal of Vacuum Science & Technology B*, vol. 12, no. 6, pp. 3857–3862, 1994.
- [78] G. Wallraff, J. Hutchinson, W. Hinsberg, F. Houle, and P. Seidel, "Kinetics of thermal and acid-catalyzed deprotection in deep-uv resist materials," *Microelectronic Engineering*, vol. 27, no. 1âĂŞ4, pp. 397 – 400, 1995.

- [79] F. A. Houle, W. D. Hinsberg, M. Morrison, M. I. Sanchez, G. Wallraff, C. Larson, and J. Hoffnagle, "Determination of coupled acid catalysis-diffusion processes in a positive-tone chemically amplified photoresist," *Journal of Vacuum Science & Technology B*, vol. 18, no. 4, pp. 1874–1885, 2000.
- [80] G. M. Perera, Y. N. Pandey, A. A. Patil, G. E. Stein, and M. Doxastakis, "Reaction Kinetics in Acid-Catalyzed Deprotection of Polymer Films," *Journal* of Physical Chemistry C, vol. 116, pp. 24706–24716, NOV 22 2012.
- [81] A. A. Patil, Y. N. Pandey, M. Doxastakis, and G. E. Stein, "Characterizing acid diffusion lengths in chemically amplified resists from measurements of deprotection kinetics," *Journal of Micro/Nanolithography, MEMS, and MOEMS*, vol. 13, no. 4, p. 043017, 2014.
- [82] M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, "Anomalous diffusion of probe molecules in polystyrene: Evidence for spatially heterogeneous segmental dynamics," *Macromolecules*, vol. 28, no. 24, pp. 8224–8232, 1995.
- [83] B.-G. Wang, T. Yamaguchi, and S.-I. Nakao, "Solvent diffusion in amorphous glassy polymers," *Journal of Polymer Science*, *Part B: Polymer Physics*, vol. 38, no. 6, pp. 846–856, 2000. cited By 40.
- [84] D. B. Hall and J. M. Torkelson, "Small molecule probe diffusion in thin and ultrathin supported polymer films," *Macromolecules*, vol. 31, no. 25, pp. 8817– 8825, 1998.
- [85] D. Ehlich and H. Sillescu, "Tracer diffusion at the glass transition," Macromolecules, vol. 23, no. 6, pp. 1600–1610, 1990.

- [86] D. B. Hall and J. M. Torkelson, "Small molecule probe diffusion in thin and ultrathin supported polymer films," *Macromolecules*, vol. 31, pp. 8817–8825, DEC 15 1998.
- [87] D. Hall, K. Hamilton, R. Miller, and J. Torkelson, "Translational and rotational diffusion of probe molecules in polymer films near T-g: Effect of hydrogen bonding," *Macromolecules*, vol. 32, pp. 8052–8058, NOV 30 1999.
- [88] M. F. Cronin, T. G. Adams, T. H. Fedynyshyn, J. H. Georger, Jr., J. M. Mori, R. F. Sinta, and J. W. Thackeray, "Investigation of onium salt type photoacid generators in positive duv resist systems," 1994.
- [89] T. Itani, H. Yoshino, M. Fujimoto, and K. Kasama, "Photoacid bulkiness effect on dissolution kinetics in chemically amplified deep ultraviolet resists," *Journal* of Vacuum Science & Technology B, vol. 13, no. 6, pp. 3026–3029, 1995.
- [90] B. D. Vogt, S. Kang, V. M. Prabhu, E. K. Lin, S. K. Satija, K. Turnquest, and W.-l. Wu, "Measurements of the reaction-diffusion front of model chemically amplified photoresists with varying photoacid size," *Macromolecules*, vol. 39, no. 24, pp. 8311–8317, 2006.
- [91] G. Ceccorulli, M. Pizzoli, and M. Scandola, "Composition dependence of the glass transition temperature of polymer-diluent systems: 1. Experimental evidence of a dual behaviour in plasticized PVC," *Polymer*, vol. 28, pp. 2077–2080, Nov. 1987.
- [92] M. Scandola, G. Ceccorulli, and M. Pizzoli, "Composition dependence of the glass transition of polymer-diluent mixtures: 2. Two concomitant glass transition processes as a general feature of plasticized polymers," *Polymer*, vol. 28, pp. 2081–2084, Nov. 1987.

- [93] C. J. Ellison, R. L. Ruszkowski, N. J. Fredin, and J. M. Torkelson, "Dramatic reduction of the effect of nanoconfinement on the glass transition of polymer films via addition of small-molecule diluent," *Phys. Rev. Lett.*, vol. 92, p. 095702, Mar 2004.
- [94] R. Zorn, M. Monkenbusch, D. Richter, A. AlegrAŋa, J. Colmenero, and B. Farago, "Plasticizer effect on the dynamics of polyvinylchloride studied by dielectric spectroscopy and quasielastic neutron scattering," *The Journal of Chemical Physics*, vol. 125, p. 154904, Oct. 2006.
- [95] D. Bingemann, N. Wirth, J. Gmeiner, and E. A. Rassler, "Decoupled Dynamics and Quasi-Logarithmic Relaxation in the PolymerâĹŠPlasticizer System Poly(methyl methacrylate)/Tri-m-cresyl Phosphate Studied with 2d NMR," *Macromolecules*, vol. 40, pp. 5379–5388, July 2007.
- [96] P. J. Hains and G. Williams, "Molecular motion in polystyrene-plasticizer systems as studied by dielectric relaxation," *Polymer*, vol. 16, pp. 725–729, Oct. 1975.
- [97] M. F. Vincent, S. G. Kazarian, and C. A. Eckert, "Tunable diffusion of D20 in CO2-swollen poly(methyl methacrylate) films," *AIChE Journal*, vol. 43, pp. 1838–1848, July 1997.
- [98] B. R. Chapman, C. R. Gochanour, and M. E. Paulaitis, "CO2-Enhanced Diffusion of Azobenzene in Glassy Polystyrene near the Glass Transition," *Macromolecules*, vol. 29, pp. 5635–5649, Jan. 1996.
- [99] F. Urbach, "The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids," *Phys. Rev.*, vol. 92, pp. 1324–1324, Dec 1953.

- [100] A. Pawloski, Christian, and P. Nealey, "A standard addition technique to quantify photoacid generation in chemically amplified photoresist," *Chemistry of materials*, vol. 13, pp. 4154–4162, Nov 2001.
- [101] A. Pawloski and P. Nealey, "Effect of photoacid generator concentration on sensitivity, photoacid generation, and deprotection of chemically amplified resists," *Journal of vacuum science & technology B*, vol. 20, pp. 2413–2420, Nov-dec 2002.
- [102] A. Pawloski, Christian, and P. Nealey, "The multifunctional role of base quenchers in chemically amplified photoresists," *Chemistry of materials*, vol. 14, pp. 4192–4201, Oct 2002.
- [103] T. Tan, V. Kudryashov, and B. Tan, "Ft-ir study of a chemically amplified resist for x-ray lithography," *Applied Spectroscopy*, vol. 57, no. 7, pp. 842–849, 2003. cited By 6.
- [104] J. L. Keddie, R. A. L. Jones, and Cory, "Size-dependent depression of the glasstransition temperature in polymer-films," *Europhysics letters*, vol. 27, pp. 59–64, JUL 1 1994.
- [105] J. L. Keddie, R. A. L. Jones, and R. A. Cory, "Interface and surface effects on the glass-transition temperature in thin polymer films," *Faraday Discuss.*, vol. 98, pp. 219–230, 1994.
- [106] M. K. Mundra, C. J. Ellison, P. Rittigstein, and J. M. Torkelson, "Fluorescence studies of confinement in polymer films and nanocomposites: Glass transition temperature, plasticizer effects, and sensitivity to stress relaxation and local polarity," *The European Physical Journal Special Topics*, vol. 141, no. 1, pp. 143–151, 2007.

- [107] R. A. Ferguson, C. A. Spence, E. Reichmanis, L. F. Thompson, and A. R. Neureuther, "Investigation of the exposure and bake of a positive acting resist with chemical amplification," vol. 1262, pp. 412–424, SPIE, 1990.
- [108] B. Jung, M. Chandhok, T. R. Younkin, C. K. Ober, and M. O. Thompson, "Time dependent behavior of chemically amplified resist characterized under sub-millisecond post exposure bake," *Journal of Photopolymer Science and Technology*, vol. 24, no. 5, pp. 487–490, 2011.
- [109] B. Jung, J. Sha, F. Paredes, M. Chandhok, T. R. Younkin, U. Wiesner, C. K. Ober, and M. O. Thompson, "Kinetic Rates of Thermal Transformations and Diffusion in Polymer Systems Measured during Sub-millisecond Laser-Induced Heating," ACS Nano, vol. 6, pp. 5830–5836, JUL 2012.
- [110] B. Jung, P. Satish, D. N. Bunck, W. R. Dichtel, C. K. Ober, and M. O. Thompson, "Laser-induced sub-millisecond heating reveals distinct tertiary ester cleavage reaction pathways in a photolithographic resist polymer," ACS Nano, vol. Article ASAP, 2014.
- [111] S. N. Vouyiouka, E. K. Karakatsani, and C. D. Papaspyrides, "Solid state polymerization," *Progress in Polymer Science*, vol. 30, pp. 10–37, Jan. 2005.
- [112] J. T. Bendler and M. F. Shlesinger, "Derivation of the Kohlrausch-Williams Watts decay law from activation-energy dispersion," *Macromolecules*, vol. 18, no. 3, pp. 591–592, 1985.
- [113] D. Hall, J. Hooker, and J. Torkelson, "Ultrathin polymer films near the glass transition: Effect on the distribution of alpha-relaxation times as measured by second harmonic generation," *Macromolecules*, vol. 30, pp. 667–669, FEB 10 1997.

- [114] A. J. Berro, A. J. Berglund, P. T. Carmichael, J.-S. Kim, and J. A. Liddle, "Super-resolution Optical Measurement of Nanoscale Photoacid Distribution in Lithographic Materials," ACS NANO, vol. 6, pp. 9496–9502, NOV 2012.
- [115] H. Ito, "Chemical amplification resists for microlithography," in Microlithography - Molecular Imprinting, vol. 172 of Advances in Polymer Science, pp. 37– 245, McGrow Hill, 2005. This is a comprehensive review of chemical amplification technology.
- [116] M. D. Stewart, M. H. Somervell, H. V. Tran, S. V. Postnikov, and C. G. Willson, "Study of acid transport using IR spectroscopy and SEM," in Advances in Resist Technology and Processing XVII, Pts 1 and 2 (Houlihan, F. M., ed.), vol. 3999 of Proceedings of the Society of Photo-optical Instrumentation Engineers (SPIE), pp. 665–674, 2000. 17th Annual SPIE Conference on Advances in Resist Technology and Processing, Santa Clara, CA, FEB 28-MAR 01, 2000.
- [117] T. Kozawa, S. Tagawa, J. J. Santillan, and T. Itani, "Impact of nonconstant diffusion coefficient on latent image quality in 22 nm fabrication using extreme ultraviolet lithography," *Journal of Photopolymer Science and Technology*, vol. 21, no. 3, pp. 421–427, 2008.
- [118] D. S. Fryer, P. F. Nealey, and J. J. de Pablo, "Scaling of T-g and reaction rate with film thickness in photoresist: A thermal probe study," *Journal of Vacuum Science & Technology B*, vol. 18, pp. 3376–3380, NOV-DEC 2000.
- [119] D. L. Goldfarb, M. Angelopoulos, E. K. Lin, R. L. Jones, C. L. Soles, J. L. Lenhart, and W. L. Wu, "Confinement effects on the spatial extent of the reaction front in ultrathin chemically amplified photoresists," *Journal of Vacuum Science & Technology B*, vol. 19, pp. 2699–2704, NOV-DEC 2001.

- [120] D. S. Fryer, S. Bollepali, J. J. de Pablo, and P. F. Nealey, "Study of acid diffusion in resist near the glass transition temperature," *Journal of Vacuum Science & Technology B*, vol. 17, pp. 3351–3355, NOV-DEC 1999.
- [121] I. M. Sokolov, "Models of anomalous diffusion in crowded environments," Soft Matter, vol. 8, pp. 9043–9052, 2012.
- [122] T. H. P. Chang, "Proximity Effect In Electron-Beam Lithography," Journal Of Vacuum Science & Technology, vol. 12, no. 6, pp. 1271–1275, 1975.
- [123] G. Owen, "Methods For Proximity Effect Correction In Electron Lithography," Journal Of Vacuum Science & Technology B, vol. 8, pp. 1889–1892, NOV-DEC 1990.
- [124] E. Croffie, M. S. Cheng, and A. Neureuther, "Moving boundary transport model for acid diffusion in chemically amplified resists," *Journal of Vacuum Science* & Technology B, vol. 17, pp. 3339–3344, NOV-DEC 1999.
- [125] W. D. Hinsberg, F. A. Houle, G. M. Poliskie, D. Pearson, M. I. Sanchez, and H. Ito, "Product volatilization as a probe of the physics and chemistry of latent image formation in chemically amplified resists," *Journal of Physical Chemistry* A, vol. 106, pp. 9776–9787, OCT 24 2002.
- [126] E. K. Lin, W.-l. Wu, and S. K. Satija, "Polymer interdiffusion near an attractive solid substrate," *Macromolecules*, vol. 30, no. 23, pp. 7224–7231, 1997.
- [127] S. V. Postnikov, Transport properties of photogenerated acid and silylating agent in polymer films. PhD thesis, 1999. Copyright - Copyright UMI - Dissertations Publishing 1999; Last updated - 2014-01-21; First page - n/a; M3: Ph.D.

[128] E. A. G. J. Brandrup, E. H. Immergut, ed., Polymer Handbook. Wiley Interscience, 2003.

## Appendix A Appendix

	Tf						Tf + DOP					
$T (^{\circ}C)$	4		2		1		4		2		1	
	Ex	Sim	Ex	Sim	Ex	Sim	Ex	Sim	Ex	Sim	Ex	Sim
70	300	221	900	575	1800	2186	120	94	300	295	900	927
80	60	58	120	103	600	523	30	24	60	48	120	125
90	10	10	30	43	60	70	10	5	15	14	30	32
T (°C)	PFBS						$\mathbf{PFBS} + \mathbf{DOP}$					
	4		2		1		4		2		1	
	Ex	Sim	Ex	Sim	Ex	Sim	Ex	Sim	Ex	Sim	Ex	Sim
70	1800	1234	2700	1987	72000	10045	300	295	600	633	2700	2404
80	300	295	600	766	1800	1357	60	64	120	138	300	393
90	45	36	122	166	300	324	10	9	30	25	45	64

Table A.1: Time (sec) required for 50% deprotection. Sim = Simulation, Ex = Ex-periment.

Furthermore, several studies suggest that plasticizers induce a "universal" behavior where  $\gamma$  values coincide for the same relaxation times. We plot  $\tau$  versus  $\gamma$  in Figure A.1 to test for these correlations, and find they are only present in the PFBS system.



Figure A.1: Correlation plot for  $\tau$  vs.  $\gamma$  in each formula.