# **Recent Advances in a Molecular Level Lithography Simulation**

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# ABSTRACT

Computer simulation of microlithography is a valuable tool for both optimization of current processes and development of advanced techniques. The capability of a computer simulation is limited by the accuracy of the physical model for the process being simulated. The post exposure bake (PEB) of a deep-ultraviolet resist is one process for which an accurate physical model does not exist. During the PEB of a deep-ultraviolet resist, mass transport of photogenerated acid allows a single acid molecule to catalyze several deprotection reactions. Unfortunately, lateral transport of acid into unexposed regions of the resist complicates control over the critical dimension of printed features. An understanding of the factors that contribute to acid mobility would allow resist manufacturers to tailor resist transport properties to their needs. Molecular level models are particularly valuable when attempting to examine mechanistic phenomena and offer the best possibility of accurately predicting lithographic performance based upon the chemical formulation of a resist. This work presents a new, molecular scale simulation of the acid generation and transport process.

Keywords: Acid diffusion, post exposure bake, computer simulation, molecular model

# **I. INTRODUCTION**

Computer simulation of microlithography has proven to be a valuable tool for both optimization of current processes and development of advanced techniques. The capability of a computer simulation is limited by the accuracy of the physical model for the particular process. For example, there is great confidence in current ultraviolet exposure simulations because they are based on a firm understanding of the mechanism by which radiation propagates through matter. Knowledge of parameters such as exposure wavelength and the indices of refraction of the resist and substrate make it possible to accurately calculate the exposure energy deposited within any volume element of a photoresist film. Unfortunately, exposure is the only major step in modern photolithography for which such a rigorous model currently exists. Other unit processes in photolithography such as post exposure bake (PEB) and development are much less rigorously understood and accurate simulation of these steps relies heavily upon empiricism. An example of this is the conventional method of simulating acid transport in chemically amplified (CA) photoresists during the PEB. The usual approach is to subject the initial distribution of photogenerated acid to a Fickian diffusion model by solving Fick's diffusion equation. Describing the distribution of acid as a function of PEB time requires knowledge of a diffusion coefficient for acid in the photoresist. This diffusion coefficient is often obtained by fitting lithographic results to the results of a Fickian diffusion simulation. Unfortunately, diffusion coefficients obtained in this manner are significantly larger than those obtained by more direct experimental investigation. For example, acid diffusion coefficients on the order of  $10^{-4}$  to  $10^{-5}$  µm<sup>2</sup> s<sup>-1</sup> are consistent with Fickian models of lithographic performance, while recent experimental evidence reveals that the diffusion coefficient of photogenerated acid in poly(phydroxystyrene) (PHS), a typical deep-ultraviolet (DUV) photoresist resin, is less than  $10^{-8} \mu m^2 s^{-1}$  at typical PEB temperatures, as reported in an accompanying article.<sup>1</sup> This discrepancy is an indication that a simple Fickian diffusion model does not adequately describe the transport of acid in chemically amplified resists.

A description of acid transport based on propagation of a reaction front was recently provided.<sup>2,3</sup> This model postulates local enhancement of acid mobility due to the generation of excess but transient free volume. The excess free volume is created when volatile by-products of the resin deprotection reaction leave the film, and this excess free volume persists for a finite time that is dependent upon both the polymer resin and the temperature of the PEB. The effect of this free volume relaxation is to immobilize a fraction of the acid such that the concentration of acid in the advancing reaction front is rapidly depleted until the front ceases to propagate. Croffie, Cheng and Neureuther have simulated this effect, including both polymer relaxation effects and a locally enhanced acid diffusion.<sup>4</sup>

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Molecular models are particularly valuable when attempting to examine mechanistic phenomena and offer the possibility of predicting changes in lithographic performance that result from changes in the chemical formulation of a resist. Our ultimate goal is to develop a complete molecular model based upon fundamental and measurable parameters that includes all processing steps. Such a model could predict lithographic performance as a function of resin molecular weight and polydispersity, developer concentration, polymer free volume, residual casting solvent, PAG loading, and other such basic properties. Before a complete model of this sort can be assembled, it is necessary to expand our comprehension of each unit process in the sequence, namely, spincoat and prebake, UV exposure, post exposure bake, and development. Of these, only the exposure step is well understood. The spincoat and prebake processes have been studied,<sup>5</sup> but these processes are complicated by such phenomena as evaporation of casting solvent <sup>6,7,8</sup> and the possibility for chain conformational effects. A molecular model for the development step has yielded valuable insight into the mechanism of dissolution of phenolic polymers in aqueous base developer.<sup>9,10,11,12</sup> This molecular model has provided explanations for phenomena such as the critical base strength required for development rate and such parameters as resin pKa and developer concentration. This paper describes our approach to modeling the post exposure bake step at the molecular level.

## **II. DESCRIPTION OF MOLECULAR MODEL**

## A. Generation of a Lattice Model for the Resist Film

Our approach to molecular modeling is to represent the resist film as a three-dimensional cubic lattice. The molecular components of the resist are represented as individual cells in the lattice. Every molecule is considered individually (see Figure 1). Each lattice cell corresponds in size to a single repeat unit of the polymer. (A lattice cell represents a cubic volume that is approximately 0.7 nm on a side.) In the work presented here, each cell contains either a polymer repeat unit, a photoacid generator (PAG) molecule, a photoreacted PAG molecule (i.e., an acid/counterion pair), or a unit of free volume. Other possible lattice occupants include residual casting solvent molecules and basic additives that are often used to improve resist performance. The fixed size of each cell determines the number of cells required in the simulation lattice. For example, simulating a 400 nm pitch resist feature in a 500 nm thick resist film requires a lattice that is 560 cells wide and 700 cells high. The third lattice dimension is chosen to maximize the sampling space of the simulation while conserving computing time. A typical value for the third lattice dimension is 100 cells.



**Figure 1**. Lattice representation of a resist film, where every molecule is considered individually. Some lattice cells are strung together to represent polymer chains, others are occupied by photoproducts. Vacant lattice sites represent the free volume of the resist film. This example is two-dimensional and contains 16 cells. A lattice used in simulation is three-dimensional and may contain tens of millions of cells.

Many chemically amplified DUV resists derive their functionality from the acid-catalyzed cleavage of a blocking group to expose a phenolic site on the polymer chain. Many chemical formulations are possible; one that has been widely studied comprises poly(*p*-hydroxystyrene) (PHS) chains that are partially blocked by *t*-butoxycarbonyl groups (*t*-BOC). This is the resist formulation considered in this work. The overall acid-catalyzed deblocking reaction is shown below in Figure 2.



Figure 2. Acid-catalyzed deprotection of t-BOC to produce PHS

In the molecular model, a polymer chain is represented on a lattice as a series of cells that are strung together, where each cell represents a repeat unit and adjacent repeat units share a cell face. All repeat units are not identical; blocked repeat units are significantly larger than unblocked PHS repeat units. This can be easily seen by comparing the space-filling models of the two monomer repeat units shown in Figure 3. These graphics were generated using HyperChem® (Hypercube, Inc.); the radius of the overlapping spheres is the Van der Waal's radius of the atoms.



Figure 3. Space-filling representations of monomer repeat units. PHS (a) is approximately half the size of t-BOC styrene (b).

The additional volume associated with *t*-BOC styrene repeat units (approximately twice the volume of a PHS repeat unit) is represented by a pendant cell attached to the linear polymer backbone, as shown in Figure 4. During the PEB simulation, the attached *t*-BOC styrene sites are converted into PHS sites by simply removing the pendant group (i.e., converting it to a unit of free volume).



**Figure 4**. Three-dimensional lattice representation of a partially blocked polymer chain. There are 20 repeat units in this example, 25% of which are blocked.

Formation of the resist lattice occurs in several steps. The fraction of lattice cells to be occupied by each entity may be specified, given the desired polymer free volume and blocking fraction, along with resist PAG loading. Creation of the resist lattice begins by partially filling an empty lattice of appropriate dimensions with straight polymer chains of specified molecular weight (degree of polymerization) and polydispersity. This filling process halts when the desired volume fraction of polymer chain backbones is reached. The system of straight chains is then allowed to relax by simulated reptation through the unfilled fraction of the lattice. This "slithering snake" motion may occur when a void cell is located at one end of a randomly chosen polymer chain, and it has the effect of introducing bends into the polymer chains. Periodic boundary conditions are applied in the horizontal (x, y) directions to remove the effects of the finite lattice size in these directions. Impenetrable boundary conditions are applied in the vertical (z) direction to simulate the top and bottom of the resist film. The reptation process continues for many steps until the entire lattice is at equilibrium and additional steps do not change the average properties of the lattice. This occurs when the void spaces are uniformly distributed throughout the lattice and the polymer chains have relaxed to a random conformation. To determine when the polymer system has relaxed to a fully random configuration, the mean-squared end-to-end distance ( $\langle R^2 \rangle$ ) and the mean-squared radius of gyration ( $\langle R_g^2 \rangle$ ) are periodically calculated. The end-to-end distance of a polymer is simply the absolute distance between ends of the chain, while the radius of gyration is the root mean square distance of each monomer from the center of mass of the entire chain. Prior to equilibration, the ratio  $\langle R^2 \rangle / \langle R_g^2 \rangle$  is at a maximum because the polymer chains are fully extended. The chains relax from their elongated conformation during the equilibration process causing the ratio  $\langle R^2 \rangle / \langle R_g^2 \rangle$  to approach an asymptotic value that is in close agreement with the theoretical prediction of six.<sup>13</sup> This method of simulating an equilibrated configuration of linear polymer chains in a lattice model has been described elsewhere in greater detail.<sup>12,14,15,16</sup>

The equilibration process populates the lattice with a random configuration of polymer cells that have been strung together in linear chains of the desired polydispersity. Attachment of t-BOC pendant groups is accomplished by randomly selecting a vacant cell. An adjoining cell is then chosen at random, and if the adjoining cell is part of a polymer backbone (not a void) and contains no pendant groups, then the vacant cell is converted into a pendant group and attached to the backbone cell. If the adjoining cell is not part of a polymer backbone, or if another pendant group is already attached at that location, the entire move is rejected and another vacant cell is chosen at random. This process is continued until the desired average degree of blocking is met for the entire lattice. A simple two-dimensional example of this process is shown in Figure 5.



**Figure 5**. Two-dimensional example of steps in the attachment of pendant groups. a) Random configuration of linear chains before attachment of any pendant groups. b) Pendant group attachment in progress, showing four attempted moves. Move 1 is rejected because a pendant may not attach to a void cell. Move 3 is rejected because a pendant may not attach to a backbone unit that already has a pendant. Moves 2 and 4 are allowed. c) Resulting lattice configuration after these moves.

The "randomness" of the configuration of the polymer chains and their pendant groups is maintained during the process of adding pendant cells by selecting void cells at random, and then selecting a direction of attachment at random. (This assumes a mean field approximation that the voids are randomly distributed throughout the lattice prior to the blocking process.) Due to the random nature of this process, every single polymer chain does not have an identical degree of blocking. A sample blocking distribution is given in Figure 6, which shows the frequency of occurrence of blocking fractions for a system of  $2.6 \times 10^4$  polymer chains, each 25 units long. In this simulation, a desired blocking fraction of 0.25 was specified. It can be seen that a range of blocking fractions exists in the simulation. Photoresists generally comprise random copolymers, and as such consist of individual chains with a dispersity of blocking fractions much like that shown in Figure 6.



**Figure 6.** Sample blocking distribution for a lattice containing  $2.6 \times 10^4$  chains, each with 25 repeat units. The targeted blocking fraction was 0.25.

The next step in the creation of the photoresist lattice is to insert PAG molecules into the matrix. This is accomplished by choosing vacant cells at random and assigning them to be PAG molecules. This process continues until the lattice is populated by the desired fraction of PAG species (typically 1 - 5 percent of all sites). At this point, the lattice contains an equilibrated configuration of polymer chains with an appropriate number of pendant groups, PAG molecules, and void spaces. This represents the state of a photoresist film immediately prior to exposure.

The exposure process converts a proportion of the PAG molecules into proton/counterion pairs. The probability of a photoreaction in any volume element is considered to be proportional to the amount of radiation that is absorbed at that given location in the film. Mask patterns will cause variations in exposure across the film, and thin film interference effects (standing waves) cause exposure variations as a function of depth into the film. These phenomena are well understood, and several commercially available software packages can be used to calculate exposure energy as a function of film position. The software package Prolith® (Finle Technologies) was used to simulate exposure of photomask patterns in this work. Prolith is capable of calculating the relative amount of unreacted PAG that remains after exposure. Conversion of the PAG in the lattice proceeds according to Equation 1, below.

$$\varphi_{CONV}(x, y, z) = 1 - \Theta(x, y, z) \tag{1}$$

Here,  $\varphi_{CONV}(x, y, z)$  is the probability of conversion at the (x, y, z) location in the film, and  $\Theta(x, y, z)$  is the relative amount of unphotoreacted PAG obtained from Prolith. In the interest of clarity, this presentation is limited to simulations in which conversion is a function of x (horizontal position) and z (depth in resist film), but not y (second horizontal dimension), as would be the case for a pattern of lines and spaces. However, three-dimensional PEB simulations can readily be performed without any significant increase in computing time or complexity of the calculations.<sup>17</sup> An example of the process of converting PAG to acid is shown in Figure 7 for a 500 nm thick film exposed at 248 nm with a dose of 12.8 mJ cm<sup>-2</sup>. The simulation was based on a one-dimensional binary mask with a 200 nm line on a 400 nm pitch, and the lattice was 560 cells wide, 700 cells tall, and 100 cells deep. After the PAG species have been converted, the resist lattice represents the state of a photoresist immediately after exposure. This is a molecular level representation of the latent image of photogenerated acid.



**Figure 7**. (a) Relative amount of converted PAG as simulated by Prolith. (b) Resulting distribution of acid in the resist lattice, averaged over 100 cells in the third lattice dimension (*y*). In these plots, dark areas indicate a high concentration of photogenerated acid.

#### B. Transport of Acid During the Post Exposure Bake

The next lithographic step is the post exposure bake. In this process the temperature of the photoresist film is raised, the acid migrates through the film and catalyzes deblocking reactions. Long post exposure bakes lead to an increase in CD in positive-tone chemically amplified resists.<sup>18</sup> This has been attributed to diffusion of photogenerated acid through the resin.<sup>19</sup> However, the diffusion coefficient of acid in PHS has been measured directly<sup>1</sup> and it is below  $10^{-8} \mu m^2/s$ , far too small to account for the observed linewidth spread. Clearly, simple diffusion cannot explain the linewidth spread that is observed. A better understanding of the underlying mechanism of CD bias is required. It is interesting to note that linewidth spread does not continue indefinitely. Most linewidth spread occurs rapidly and then the rate of spread decreases dramatically. Again,

simple diffusion is unable to account for this observation. Not only does the acid undergo a much larger degree of mass transport than expected, but that acid transport slows drastically after a short time.

It is well known that acidic species migrate through the resist and catalyze reactions, but the exact mechanism of acid transport remains unclear. If acid moves alone as a proton ( $H^+$ ), its transport properties would be much different than if the acid moves in association with its conjugate base counterion. It is necessary to know the effective sphere of influence of an acid - the size of the region around a conjugate base to which the proton is effectively confined. To the extent that a proton must associate with its conjugate base (anion), a smaller sphere of influence is expected. The bulky anion will be relatively immobile due to excluded volume restrictions and association with this ion will limit the motion of the acid. If, on the other hand, the two do not associate with one another, the proton would have a much greater mobility and a larger amount of acid motion would be expected. A certain degree of associated transport is implied by the experimental observation that acid mobility is much lower when generated from photoacid generator molecules that produce large conjugate bases.<sup>20</sup> Shi has provided analysis of the effects of both coulomb interactions and acid-base equilibria upon acid diffusion.<sup>21</sup> Electrostatic interactions in the photoresist were investigated via calculation of the order of 1 nm, which implies that only charged species within a 1 nm radius will affect transport of a proton ( $H^+$ ). Analysis of the effect of acid-base equilibrium resulted in the conclusion that these equilibrium effects are essentially negligible for very strong acids, and it was determined that the motion of protons and their counterions is strongly correlated.

The interaction between a proton and its conjugate base was further probed with a quantum mechanical simulation program. The results shown here were generated with HyperChem®, Hypercube Inc. Such programs perform geometric (conformational) optimization of a molecule by computing the electronic configuration, and can calculate the three-dimensional electrostatic potential around the optimized structure. Simulations were performed for several conjugate base anions, one of which is shown in Figure 8. This graphic is the result of the simulation of an isolated system with a dielectric constant of unity, where effects of a bulk medium and/or neighboring molecules were ignored. The effect of a larger dielectric constant can be seen from the electrostatic potential of a point charge as given in Equation 2, below.

$$\Phi = \frac{z_i e}{4\pi\varepsilon_0 \varepsilon_r r} \tag{2}$$

Here,  $z_i$  is the charge on particle *i*,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the relative permittivity (or dielectric constant) of the medium, and *r* is the distance of separation of the two charged particles in that medium. Thus, in a dielectric medium, the magnitude of the potential will be reduced by a factor of  $\varepsilon_r$ .

The separation between contour levels in Figure 8 is 1.0 V. In the absence of a dielectric medium, a proton (with unit charge) experiences an energy difference between contour levels of approximately  $1.6 \times 10^{-19}$  J. For comparison, thermal (kT) energy at 100 °C is  $5.2 \times 10^{-21}$  J. For an approximate dielectric constant of 2.5,<sup>22</sup> the energy difference would be  $6.4 \times 10^{-20}$  J. The Boltzmann probability that a proton will be at a higher energy contour drops off by a factor of  $2 \times 10^5$  from contour to contour (at 100 °C). This is in agreement with the conclusion of Shi, that the proton will remain in very close proximity to its conjugate base, and diffusion of the acid is therefore strongly limited by the diffusion of the counterion. The regions of highest probability (i.e., most negative potential) in Figure 8 are indicated by "H-stars". As expected, these regions surround the highly electronegative oxygen atoms. It should be noted that the figure displays a single two-dimensional slice through the three-dimensional electrostatic potential field, and some irregularities in the field result merely from the slice plane that was chosen.



**Figure 8**. Electrostatic potential map for the perfluorobutanesulfonate anion, the structure of which is given below. The curves represent contours of equal potential as determined using an AM1 self-consistent field; the separation between contours is 1.0 V. The 2-D slice shown is for a plane containing the carbon-sulfur bond and one of the sulfur-oxygen bonds. The regions of lowest potential in this plane are shown by "H-stars".

perfluorobutanesulfonate anion



The very strong attraction between the proton and its counterion means that protons must reside in close proximity to their conjugate base. Photogeneration of acid by radiation will cause a small but finite separation of charge, as will regeneration of acid catalyst during the deblocking reaction. However, the strong coulombic interaction will rapidly reestablish the union of the proton/counterion pair. Mobility of the proton will be greatly decreased by the bulkiness of the counterion because the pair must move together through the free volume of the resist film. The lattice model represents this free volume restriction by allowing photoproduct units to move only into void cells.

Motion of cells on the lattice is limited to photoproducts and unconverted PAG. These units may only move by trading places with a neighboring void cell; the void cell moves by default whenever this occurs. Motion of photoproducts and PAGs on the lattice proceeds in a stepwise manner. In each step, every mobile unit is examined (in random order) for the possibility of motion. First a mobile unit is randomly chosen, and then one of its 26 neighboring cells is also chosen at random. If the randomly chosen cell is a void, then the move is accepted and the unit moves into the cell and leaves behind a void cell. Otherwise the move is rejected, and another mobile unit is randomly chosen. The step is complete when all of the mobile units have been considered, and another step may be taken. Many steps are required to effect a significant degree of transport on the lattice, but it is difficult to assign a real time scale to any one of these steps due to the Monte Carlo nature of the simulation. In actuality, the real time that is represented by each step is the average time required for a photoproduct to move a distance within the resist that matches the average distance per step on the lattice. Investigation of this relationship is one area of focus for future work.

The acid molecules may catalyze reactions in *t*-BOC cells that are within a certain radius of influence. This radius must be very small due to the strong attraction between acid and counterion. On a cubic lattice each cubic cell has 6 neighbors that share a face, 12 neighbors that share an edge, and 8 neighbors that share a corner. These 26 adjacent cells constitute the "sphere of influence" of the central cell, in that they are the only cells with which the central unit has any contact. Thus, whenever a blocked site is within the sphere of influence of a photoproduct cell, a deblocking reaction occurs and the blocked site is immediately converted into a void cell. This method of simulation of intermolecular reaction is an approximation in that it does not account for reaction kinetics or alignment of reactants. It has been assumed that the time required for the deprotection reaction and the alignment of reactants is much smaller that the time simulated by one step of motion through the resist lattice. The validity of this assumption is another area of focus for future work. Ultimately, the temperature dependence of the probability of a reaction occurring within the sphere of influence can be related to the activation energy of the reaction.

Motion of the polymer chains after equilibration is not included in the work presented here. The relatively small photoproduct molecules are expected to be more mobile than the polymer chains; however, even minor polymer chain rearrangements can have a significant effect. Polymer chain motion can allow for redistribution of the free volume in a resist film, and can thus provide a diffusion pathway for an otherwise immobile molecule. Also, polymer chain relaxation will eliminate the excess free volume that is generated when volatile byproducts of the deprotection reaction leave the resist film, thereby reducing the mobility of photoproducts in the region. Both the lifetime and the amount of excess free volume generated by reaction is thus strongly dependent upon the temperature of the PEB in relation to the glass transition temperature of the polymer. The effects of void lifetime and polymer chain motion will be studied in future work.

In the absence of the halting mechanism for acid migration that is provided by polymer chain relaxation, a single photogenerated acid could deprotect the entire lattice in an infinite number of timesteps. An alternate stopping mechanism is required to avoid this result. To this end, a simple fixed catalytic chain length is imposed on each photogenerated acid. Each acid unit is thus allowed to move through the lattice voids in the stepwise manner described earlier. However, after an acid had catalyzed the set number of reactions it becomes "deactivated" and is no longer able to catalyze further reactions. Transport of the deactivated acid is still possible, but a deactivated acid unit cannot catalyze any further reactions. This artificial construct will be unnecessary when motion of polymer chains on the lattice is incorporated in the simulation.

# **III. PRELIMINARY RESULTS**

Simulation results are presented here for a 500 nm thick film under the exposure conditions presented in Figure 7. This exposure produces a distribution of acid that shows several strong standing waves. The lattice simulated here was 560 cells wide, 700 cells tall, and 100 cells deep. The lattice was generated in the manner described earlier to produce a lattice with polymer chains 25 units long and with an average blocking fraction of 25 percent. Three percent of the lattice sites were populated by PAGs and 9 percent of lattice sites were voids. Exposure of the lattice was simulated by applying the fractional

conversion shown in Figure 7. Finally, the PEB was simulated for 5000 simulation steps with a maximum catalytic chain length of 150 reactions.

The mean displacement of units, defined as the absolute distance from initial location to final location, was tracked for the simulation and is plotted in Figure 9. It is seen that a relatively large amount of transport occurs early in the simulation, but transport slows dramatically as the simulation progresses. One reason for this slowing is the fixed catalytic chain length imposed upon each acid. Once an acid has reached the maximum number of reactions it is no longer capable of generating its own transport pathways, and can therefore move only into voids that are already present in its immediate surroundings. Another reason for the decrease in rate of motion is that the longer transport pathways are statistically less probable. The probability that any given unit will be able to complete its first successful move is equal to the probability that either a void site or a blocked site will neighbor the unit. This probability is approximately equal to the fraction of lattice sites that are valid as transport pathways (i.e., sites that are either voids or blocked units). The probability that additional steps are possible is the probability that additional valid sites exist as a continuous string; the chance of this decreases exponentially with number of steps. These two effects combine to inhibit the transport of acid units over long distances.



Figure 9. Acid Transport: Mean Displacement versus Number of Simulation Steps



Figure 10. Distribution of displacement lengths after 5000 simulation steps

Figure 10 shows the distribution of net displacement distances after 5000 simulation steps. It can be seen that a wide range of migration distances occurred in the simulation, but the distribution is highly skewed toward shorter transport distances and very few units moved greater than 40 lattice sites (about 30 nm) from their initial location.

Deprotection reactions occurred in the simulation by the conversion of pendant blocking groups into voids in the vicinity of a photoproduct unit. The number of blocking groups, voids, and active acids was tracked during the simulation as a means of studying reaction progress. This data is shown in Figure 11. The simulated reaction proceeds rapidly at first as the acids react with the blocked sites in their immediate vicinity. As the simulation progresses the reaction quickly slows as the immediately available blocked sites become depleted and acids reach the maximum catalytic chain length.



Figure 11. Reaction progress: Blocked sites are converted directly to voids, leading to an increase in the free volume of the film. Each acid was allowed to cause a maximum of 150 reactions.

The spatial distributions of acids and blocked sites are shown below. Figure 12 shows the spreading of the initial concentration of acids throughout the lattice. Initially, the acids are strongly concentrated within the regions of the standing waves that received the highest energy. As the simulation progresses and the acids are allowed to move through voids, the distribution of acids broadens. Figure 13 shows the corresponding evolution of the distribution of blocked sites. Prior to the PEB, there is a uniform distribution of blocked sites through the lattice because no reactions have occurred. Shortly after the PEB begins, the appearance of standing waves becomes evident in the distribution of blocked sites.



Figure 12. Spreading of the acid distribution during the PEB. Light areas indicate a high concentration of acids. (a) Initial distribution of acids after exposure (b) After 1000 steps (c) After 2000 steps (d) Final distribution of acids after 5000 steps.



**Figure 13**. Evolution of the blocking profile during the PEB. Light areas indicate a high concentration of blocked sites. (a) Initial (uniform) distribution of blocked sites before the PEB (b) After 1000 steps (c) After 2000 steps (d) Final distribution of blocked sites after 5000 steps.

#### **IV. CONCLUSIONS AND FUTURE WORK**

Advances in computer technology make it possible to perform a molecular level simulation of the microlithography process in which every molecule is considered. The molecular level simulation presented here is capable of accurately representing any molecular weight and polydispersity of polymer resin. This is possible because polymer chains of the desired length are added directly to the lattice. Polymer blocking fractions are represented accurately up to approximately 75%, at which point the distribution of voids around each polymer chain is nearly depleted and no more voids can be added. It is possible to accurately represent any nonzero void volume, as well as any amount of residual casting solvent and any PAG loading desired. The desired numbers of these entities are added directly to the lattice. Exposure calculations are performed by Prolith© to determine the fractional conversion of PAG as a function of spatial coordinate within the lattice. The distribution of acid that is produced by exposure is then transported stepwise through the lattice according to excluded volume restrictions.

While this work demonstrates the potential of a molecular approach to PEB simulation, it is clear that much remains to be done before reliable quantitative prediction of lithographic performance is possible. Work is now directed toward development of a better understanding of the mechanism of photoproduct migration halting. It will then be possible to accommodate an appropriate algorithm into the molecular level simulation. It will also be necessary to develop a connection between the number of Monte Carlo steps and elapsed time. The ultimate goal of this work is to incorporate all modules of molecular level simulations into a single model that enables prediction of lithographic performance based upon fundamental and measurable properties of materials.

## ACKNOWLEDGMENTS

We gratefully acknowledge financial support for this work from the Semiconductor Research Corporation (contract number 2000-MJ-752), from Eastman Kodak through a graduate research fellowship, and from Intel Corporation through a graduate internship to GMS. The authors would also like to thank Dr. Isaac C. Sanchez and Matthew Stone at the University of Texas at Austin for their helpful technical discussions.

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<sup>18</sup> John Sturtevant, Steve Holmes, and Paul Rabidoux, "Post-exposure bake characteristics of a chemically amplified deep-ultraviolet resist", *Proc. SPIE, Adv. Resist Technol. Process.*, 1672, pp. 114-124, 1992.

<sup>19</sup> T. H. Fedynyshyn, J. W. Thackeray, J. H. Georger, and M. D. Denison, "Effect of acid diffusion on performance in deep ultraviolet resists", *J. Vac. Sci. Technol. B*, 12, pp. 3888-3894, 1994.

<sup>20</sup> Toshiro Itani, Hiroshi Yoshino, Masashi Fujimoto, and Kunihiko Kasama, "Photoacid bulkiness effect on dissolution kinetics in chemically amplified deep ultraviolet resists", *J. Vac. Sci. Technol. B*, 13, pp. 3026-3029, 1995.

<sup>21</sup> Xuelong Shi, "Effect of Coulomb interaction and pKa on acid diffusion in chemically amplified resists", *J. Vac. Sci. Technol. B.*, 17, pp. 350-354, 1999.

 $^{22}$  For nonmagnetic media, the dielectric constant is equal to the square of the index of refraction. The refractive index is wavelength dependent and may be estimated from the Cauchy equation. The dielectric relaxation frequency for normal alcohols is on the order of  $1 \times 10^{12} \text{ s}^{-1}$  (J. A. Saxton, R. A. Bond, G. T. Coats, and R. M. Dickinson, "Dispersion at Millimeter Wavelengths in Methyl and Ethyl Alcohols", *J. Chem. Phys.*, 37, pp. 2132-2138, 1962). It is presumed that the dielectric relaxation frequency for PHS will we equal or less than this value. At this frequency, a dielectric constant of less than 2.5 is expected. It should be noted that the local dielectric constant might be noticeably larger in the proximity of a carbonyl or alcohol functional group, for example. Nevertheless, the attraction between the proton and counterion is much stronger, and temporary separations cause by thermal motion will be rapidly eliminated. The energetic cost of charge separation is very high.

<sup>&</sup>lt;sup>10</sup> Lewis W. Flanagin, Vivek K. Singh, and C. Grant Willson, "Surface roughness development during photoresist dissolution", *J. Vac. Sci. Technol. B.*, 17, pp. 1371-1379, 1999.

<sup>&</sup>lt;sup>13</sup> K. Kremer and G. S. Crest, in *Monte Carlo and Molecular Dynamic Simulations in Polymer Science*, edited by K. Binder (Oxford University Press, New York, 1995), p. 199.