Electrostatic effects during dissolution of positive tone photoresists

Gerard M. Schmid,[a] Sean D. Burns, Pavlos C. Tsiartas, and C. Grant Willson
Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

(Received 16 July 2002; accepted 23 September 2002)

Positive tone photoresist function is based upon modulation of the dissolution rate of an acidic polymer in aqueous base developer. During dissolution, a negative surface charge accumulates at the surface of the photoresist film as acidic sites on the polymer are ionized by the basic developer. This negative surface charge causes a depletion of hydroxide ions in the developer solution immediately adjacent to the film. One effect of this phenomenon is to reduce the dissolution rate relative to rates predicted from the bulk base concentration. The depletion of base at the resist/developer interface has been studied through the application of the Poisson–Boltzmann equation and through Monte Carlo simulations. It is shown that the extent of depletion of hydroxide at the surface of the film is related to the bulk developer concentration and the local geometry of the interface. Interfacial geometry is found to be most influential on the length scale of 1–10 nm. When electrostatic effects are considered in conjunction with the equilibrium of the acid–base reaction, the fractional ionization of the surface of the film is significantly lower than previously calculated. Understanding the relationship between the acid–base equilibrium and electrostatic equilibrium represents an important step in our efforts to understand the fundamental dissolution mechanism of positive tone photoresists. © *2002 American Vacuum Society.* [DOI: 10.1116/1.1521735]

I. INTRODUCTION

Positive tone photoresist function is based upon modulation of the dissolution rate of an acidic polymer in aqueous base developer. Several empirical models for the development process are able to accurately model photoresist performance,[1] but the molecular level details of the underlying dissolution mechanism are not yet fully understood. It is clear that the mechanism by which a single molecule of a photoresist polymer dissolves consists of (at least) three separate steps (Fig. 1).[2–5] First, hydroxide ions in the developer diffuse to the polymer molecule. Next, the hydroxide ions deprotonate acidic sites on the polymer molecule via acid–base reactions. Finally, the polymer molecule moves to the bulk of the developer solution. Traditional theories for dissolution of glassy polymer films state that the process is transport limited, either in transport of the solvent to the polymer (step 1) or in transport of polymer into the bulk of the solvent (step 3).[6–8] However, the dissolution of positive tone photoresists is a very different process because the species in solution (a polyion) is different from the polymer in the film (a polyol). Chemical reactions of the basic developer solution with acidic sites on the polymer chains enable dissolution of the film. The critical ionization (CI) model for the dissolution of phenolic polymers in an aqueous base[9,10] treats photoresist dissolution as a reaction-limited process in which a critical fraction of repeat units on a given polymer chain must be ionized before the chain becomes soluble in the developer solution. The input parameters to this model are f_{CRIT}, the critical fraction of sites on a chain that must be ionized for dissolution to occur, and α, the fraction of all polymer sites exposed to the developer that are ionized at equilibrium. f_{CRIT} is a microscopic quantity; therefore, it is difficult to design an experiment that will yield an unambiguous measurement of this value.[11] However, α is a macroscopic quantity that can theoretically be calculated based upon the pK_a of the polymer and the concentration of the developer solution.

The CI model has provided a satisfying explanation for some fairly complex experimental observations. For example, the model correctly predicts that the dissolution rate is inversely related to the logarithm of the molecular weight of the polymer,[9] that the dissolution rate is essentially zero below some critical, nonzero base concentration,[9] that surface roughness increases with increasing polymer molecular weight,[12] etc. This relatively simple model also reproduces the particularly complex influence of adding salts to the developer solution: The dissolution rate increases fairly linearly with the initial addition of salt and then decreases nonlinearly at higher salt concentrations.[9]

While the CI model matches these qualitative trends very well, there have been persistent difficulties in achieving quantitative agreement with the experimentally observed dissolution rates: Simulated dissolution rates are much faster than measured values. To further understand the discrepancy between experiment and simulation, we focus our attention on the determination of α. Calculation of α results from consideration of the acid–base equilibrium between the polymer and the developer,

$$\mathrm{POH} + \mathrm{OH}^- \leftrightarrow \mathrm{PO}^- + \mathrm{H_2O}. \tag{1}$$

The equilibrium of this reaction has been estimated by[10]

$$\alpha = \frac{[\mathrm{PO}^-]}{[\mathrm{POH}]} = \frac{10^{p\mathrm{H}-pK_a}}{1+10^{p\mathrm{H}-pK_a}}. \tag{2}$$

Here, the quantities in brackets refer to concentrations of polymer repeat units that are in contact with the developer

[a]Electronic mail: schmid@che.utexas.edu

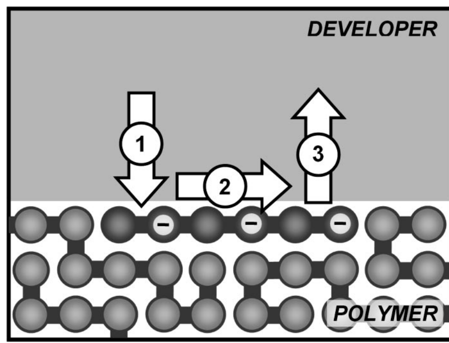

FIG. 1. Dissolution mechanism of positive tone photoresists includes (1) transport of hydroxide to polymer, (2) reaction of hydroxide with polymer, and (3) transport of polymer to developer.

solution. This analysis employs several standard approximations that are strictly valid in the limit of infinite dilution: The activity of water and the activity coefficient of the unionized polymer have been set to unity, and the activities of other species have been approximated by molar concentrations. Equation (2) is plotted in Fig. 2 for the standard developer concentration of 0.26 N in hydroxide. As shown in Fig. 2, this analysis predicts the complete ionization of the acidic polymer sites that are in contact with the developer, based upon the pK_a's of typical photoresist resin polymers. This, in turn, predicts very rapid dissolution and a process that is independent of the reaction rate. More realistic dissolution rates are simulated if the degree of ionization is reduced to the range of 0.5–0.9 by either increasing the pK_a of the simulated polymer or by decreasing the concentration of the developer solution. Decreasing α through these *ad hoc* adjustments reduces the number of chains that meet f_{CRIT} at any given time and, thus, slows the removal of chains from the film. The disagreement between simulated and experimentally observed dissolution rates suggests that Eq. (2) overestimates the ionization of the polymer surface.

The failure of the aforementioned analysis can be understood by recognizing that Eq. (2) applies to equilibrium in a homogeneous solution, but the photoresist development centers around a solid–liquid interface. A recent theoretical analysis has predicted the formation of a significant electrostatic double layer at the interface between the resist and the developer.[13] A negative charge accumulates at the surface of the film as the acidic sites on the polymer chains become ionized, but before the chains dissolve. The negative surface charge causes a depletion of hydroxide ions in the developer solution immediately adjacent to the film, such that the concentration of the base at the ionized surface can be an order of magnitude more dilute than the bulk concentration. Formation of an electrostatic double layer greatly reduces the ionization of the surface of the film by decreasing the apparent concentration of the developer solution.

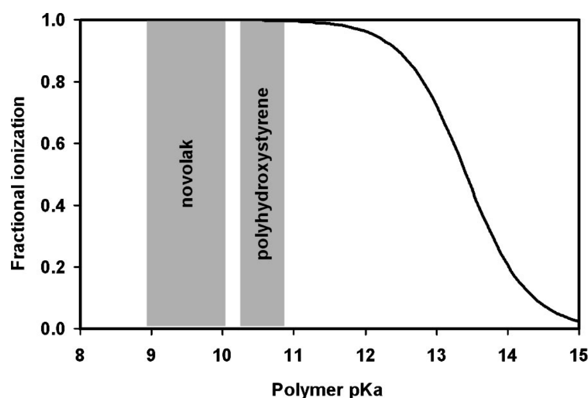

FIG. 2. Fractional ionization of acidic polymer in 0.26 N TMAH developer, calculated using Eq. (2). This simple analysis predicts complete ionization.

This work focuses on understanding how electrostatic interactions can affect the dissolution performance of positive tone photoresists. First, the Poisson–Boltzmann (PB) equation is evaluated for several situations relevant to photoresist development. The results of these calculations are discussed in terms of the potential implications for industrial photolithography. A Monte Carlo simulation of the photoresist/developer interface is then described as an extension to previously reported computer simulations for photoresist processing.[14–16] Results of this Monte Carlo implementation are presented to exemplify the distinct advantages of this approach.

II. POISSON–BOLTZMANN EQUATION

The PB equation[17] is a nonlinear second-order differential equation that can be solved to yield the electrostatic potential and ion concentration in the vicinity of a charged surface:

$$\nabla^2 \phi = \kappa^2 \sinh \phi. \tag{3}$$

Here, ϕ is the dimensionless potential, $ze_c\psi/k_bT$. The valence of the ions is represented by z, e_c is the unit of electric charge, and ψ is the electrostatic potential. κ^{-1} is the Debye screening length, given by

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 kT}{1000 e_c^2 N_A \Sigma z_i^2 [C_i]}}, \tag{4}$$

where ϵ is the dielectric constant of the medium, ϵ_0 is the vacuum permittivity, N_A is Avogadro's number, and $[C_i]$ is the molar concentration of species i. The summation is performed over all ionic components of the electrolyte solution to calculate the ionic strength. In a 0.26 M solution of tetramethylammonium hydroxide (TMAH) at room temperature, κ^{-1} is approximately 6 Å. The ion concentration ρ at a location where the electrostatic potential is ψ is given by the Boltzmann distribution

$$\rho = \rho_0 e^{-ze_c\psi/kT}, \tag{5}$$

where ρ_0 represents the ion concentration in the bulk of the solution.

Solution of the PB equation is complicated by its nonlinearity. The PB equation may be linearized in accordance with the Debye–Hückel treatment by recognizing that $\sinh \phi \sim \phi$ in the limit of $\phi \rightarrow 0$:

$$\nabla^2 \phi = \kappa^2 \phi. \tag{6}$$

The calculations presented herein were obtained by first solving the linearized PB equation [Eq. (6)], and using that

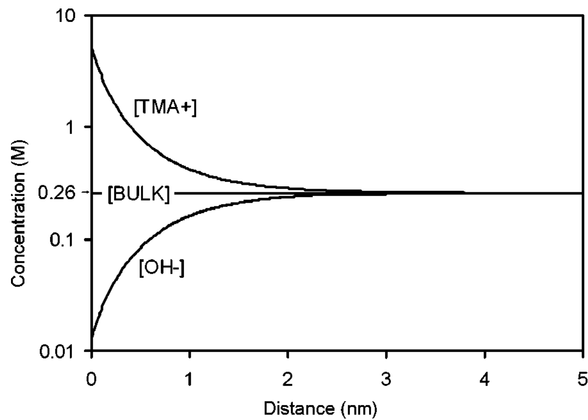

FIG. 3. Electrostatic double layer at the interface between 0.26 M TMAH aqueous solution and a charged polymer surface, calculated using the PB equation.

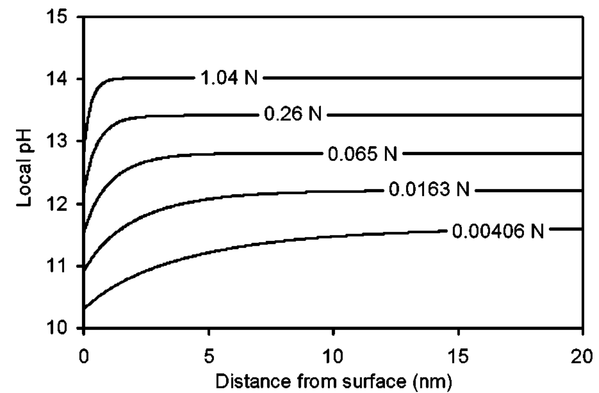

FIG. 5. Depletion of hydroxide near the interface between a charged polymer surface (ψ~77 mV) and aqueous TMAH solution as calculated using the PB equation for various TMAH concentrations.

solution as an initial estimate for solving the full, nonlinear PB equation [Eq. (3)]. In all cases, solutions were obtained by the method of successive overrelaxation.[18] Film surface boundary conditions are noted when appropriate. Additionally, the electrostatic potential was taken to be zero at large distances from the film surface, and periodic boundary conditions were applied to vertical domain boundaries.

A. Uniformly charged planar surface

The general structure of the electrostatic double layer is shown in Fig. 3 for a planar surface having a uniform potential of 77 mV, which corresponds to approximately 35% ionization of a planar polyhydroxystyrene (PHS) surface. The results presented are for an electrolyte solution of 0.26 N TMAH at room temperature. Positively charged counterions accumulate at the negatively charged surface, while the negatively charged hydroxide ions are repelled. Under these conditions, the concentration of the base at the surface has been decreased by a factor of 20 from the bulk value, and the depletion effect is still significant at a distance of 1 nm from the interface. The distinct effects of variations in surface potential and ionic strength are shown in Figs. 4 and 5. At a fixed ionic strength, varying the electrostatic potential at the interface corresponds to varying the fractional ionization of the surface of the film. Higher degrees of ionization require correspondingly higher concentrations of counterions at the interface to balance the charge. These increases in counterion accumulation at the interface are accompanied by reductions in the local concentration of base. Variations in the developer concentration have a different effect. For a fixed surface potential, lowering the ionic strength reduces the extent to which the surface charge is screened by the solution. Thus, deviations from the bulk concentration are evident at greater distances from the interface at lower ionic strengths. In practice, variations in ionic strength that result from changing the concentration of the base will alter the ionization equilibrium of the surface. The relationship between the electrostatic equilibrium and acid–base reaction equilibrium will be discussed later.

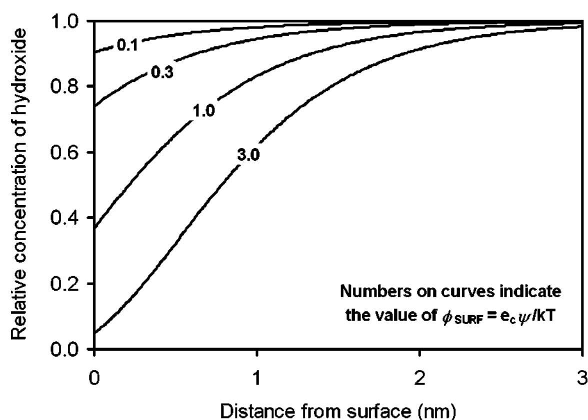

FIG. 4. PB equation results showing the depletion of hydroxide near the interface of a charged polymer surface and an aqueous 0.26 M TMAH solution.

The results given in Figs. 3–5 apply to a uniformly charged planar film—a situation that is closely approximated at the onset of development of a large area of the resist has received the same exposure dose. Under those conditions, the surface of the film is nearly planar and the distribution of ionizable sites is essentially uniform across the surface. The structure of the electrostatic double layer will be different if there is a nonuniform distribution of ionizable sites across the resist/developer interface, or if the interface is nonplanar.

B. Nonuniformly charged planar surface

Predevelopment processing of a positive tone chemically amplified photoresist includes pattern-wise irradiation followed by a postexposure bake step. This processing alters the composition of the resist in irradiated regions; specifically, protecting groups on the polymer are converted to acidic groups. Consequently, regions of the film that received a high exposure dose have a higher concentration of ionizable sites than regions that received less exposure. In a hypothetical limit, a sharp boundary separates a region containing no ionizable sites from another region that contains some finite, uniform concentration of ionizable sites, as seen in Fig. 6. Here, the region $-10 < x/h < 10$ has a uniform electrostatic

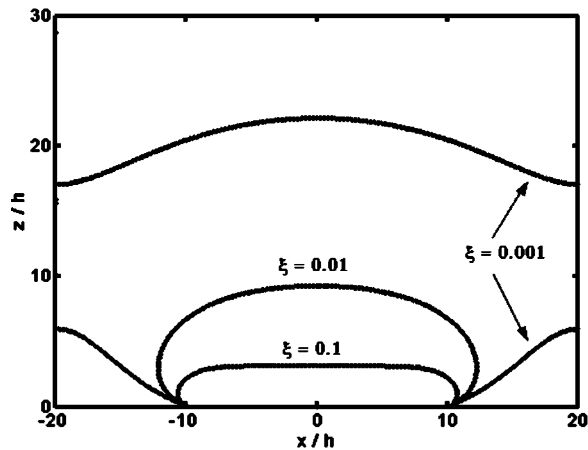

FIG. 6. Contour lines show the location where the concentration of the base has been reduced to 90% of the bulk value for a given value of $\xi = Ih^2$, where I is the molar ionic strength of the bulk solution and h is the scale of the spatial dimension in nm. The surface of the film is at $z/h = 0$, with a fixed surface potential $\psi = k_b T/e_c$ (~26 mV) for $x/h = -10$ to 10 and $\psi = 0$ elsewhere.

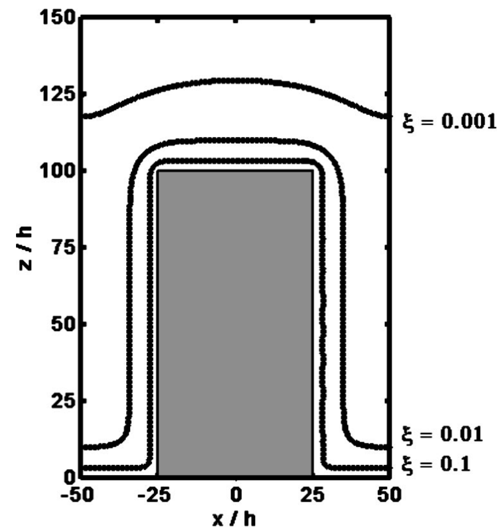

FIG. 7. Contour lines show the location where the concentration of base has been reduced to 90% of the bulk value for a given value of $\xi = Ih^2$, where I is the molar ionic strength of the bulk solution and h is the scale of the spatial dimension in nm. The resist surface exists at $z/h = 0$ as well as at the boundary of the shaded rectangle, with a fixed surface potential $\psi = k_b T/e_c$ (~26 mV).

potential (~26 mV) that corresponds to ~10% ionization of a planar PHS surface; elsewhere, the electrostatic potential is zero. The axes on the plot have been normalized to a scaling parameter h (nm), and contours on the plot show the location at which the base concentration has been reduced to 90% of the bulk value, for a given value of $\xi = Ih^2$, where I is the molar ionic strength. For example, if h is taken to be 1 nm, then the plot represents equal lines and spaces exposure with a pitch of 40 nm. In this case, $\xi = 0.1$ corresponds to a developer concentration of 0.05 M TMAH. At higher concentrations, the depletion of the base is only significant very near the charged portion of the surface. (However, the surface potential has been fixed in these calculations and, thus, the concentration of the base at the charged portion of the surface has been equally depleted in all cases to ~37% of the bulk value.) The consequence of this phenomenon in terms of imaging performance is that regions of the resist surface having a higher concentration of ionizable sites are exposed to lower concentrations of the base. It is conceivable that this might detract from the desired dissolution performance: The regions of resist that are intended to dissolve most rapidly are exposed to the lowest concentration of the developer. In practice, most chemically amplified photoresist formulations contain polymer chains that are only 25% to 50% protected. Thus, there is always a fairly high concentration of ionizable sites, even in regions that have not been exposed. In addition, the surface distribution of ionizable sites on a photoresist film will not have this sharp boundary. A more realistic representation would be a sinusoidal variation in the concentration of ionizable sites, rather than a step function.

C. Uniformly charged nonplanar surface

The electrostatic double layer will also be influenced by the presence of surface topography, including both short-range topography (surface roughness) and long-range topography (resist features). The influence of surface geometry was investigated by calculating the electrostatic double layer for a grating topography of equal lines and spaces (Fig. 7). A surface potential of approximately 26 mV was applied uniformly to the interface to isolate the effects of interfacial geometry. The axes of the plot have again been normalized to a scaling parameter h (nm), and contours on the plot show the location at which the base concentration has been reduced to 90% of the bulk value, for a given value of ξ. If h is taken to be 1 nm, then the plot represents a system of equal lines and spaces with a pitch of 100 nm. In this case, $\xi = 0.1$ corresponds to a developer concentration of 0.05 M TMAH. In regions where the local geometry of the interface is concave with respect to the film (e.g., at the base of a resist feature), the depletion of base extends further into the developer. Conversely, there is less depletion of base in regions where the interface is convex (e.g., at the top edges of a resist feature). The shape of the profiles in Fig. 7 suggests that this effect might contribute to undesirable phenomena such as corner rounding and resist feature footing. However, at the standard developer concentration, the effect is minimal except at very small dimensions ($\lesssim 5$ nm). Topography on this length scale is representative of surface roughness rather than resist features. This analysis suggests that convex protrusions from the resist surface are exposed to a higher concentration of the base than the rest of the surface. This higher concentration of the base can result in a higher degree of ionization of polymer sites within the protrusion, in which case, the protrusions would be expected to dissolve at a faster rate. In this case, it is conceivable that electrostatic interactions can minimize resist feature roughness. If the pK_a of the polymer is very low or very high, the degree of ionization of the polymer will not be affected by these relatively small changes in the base concentration. The calculations presented in Fig. 7 suggest that the influence of the

local interfacial geometry is reduced at high developer concentrations, such that all points on the surface are exposed to the same concentration of base. It should be noted that we have fixed the electrostatic surface potential independently of the base concentration at the surface. In reality, the electrostatic potential at the surface will depend upon the local degree of ionization of the surface which, in turn, is influenced by the local concentration of the base.

III. MONTE CARLO ANALYSIS

We have previously reported mesoscale Monte Carlo simulations for several of the photoresist processing steps: Film creation, exposure, postexposure bake, dissolution, and drying.[12,14–16,19] In these simulations, we have modeled the photoresist film on a three-dimensional lattice, with individual lattice sites representing specific chemical components of the film. Some of the lattice sites represent polymer repeat units; these are strung together to model polymer chains. Other lattice sites correspond to molecular components such as a photoacid generator, photogenerated acid, solvent, free volume, etc. These simulations have been used to simulate changes in resist performance that result from changes in the chemical formulation of the photoresist.

In previous simulations of photoresist development, the developer solution has been approximated as a continuum with uniform concentration. It has now been shown that this approximation introduces significant error into the ionization calculation. To address this error, a Monte Carlo approach to simulating the electrostatic double layer has been adopted. The so-called primitive model of an electrolyte[20–22] is employed, wherein the developer solution is modeled with discrete ions in a dielectric continuum of water. The polymer component is represented on a lattice, but the ions are represented off lattice so that the fine structure of the electrostatic double layer may be investigated. Off-lattice representation of the ions also enables the investigation of the effect of ionic radius on the performance of the developer. With this approach, it is possible to consider the ionization of individual polymer sites according to the pK_a of the resist polymer. The complex mechanism of surface roughness formation in the presence of the electrostatic double layer may also be studied. Here, we will discuss details of the Monte Carlo simulation, and then use the simulation to examine the dynamic ionization of an initially uncharged planar film.

A. Methods

Our treatment of the resist/developer interface approximates the resist as a three-dimensional lattice of cells, while the developer is treated as a primitive model electrolyte solution. The primitive model approximates the electrolyte solution as a system of hard sphere ions in a dielectric continuum of structureless solvent. This simplification facilitates simulation of the relatively large domains that are of interest here ($\sim 10^4 - 10^6$ nm^3). Interactions between charged species (ions and ionized polymer sites) consist of both hard sphere, excluded volume repulsions and screened Debye–Hückel interactions, summarized next:

$$u_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon_r\epsilon_0 r_{ij}} \exp(-\kappa \cdot r_{ij}) \quad \text{if} \quad r_{ij} > \sigma_i + \sigma_j;$$
$$u_{ij} = \infty \quad \text{if} \quad r_{ij} \leq \sigma_i + \sigma_j. \tag{7}$$

Here, z_i represents the charge of ion *i*, *e* is the elementary charge, ϵ_r is the relative permittivity of the dielectric (water), and ϵ_0 is the dielectric permittivity of a vacuum. The radius of separation of ions *i* and *j* is denoted as r_{ij}, and the radius of each ion is denoted by σ. These radii are taken to be the bare ion radii, except in the case of H^+, which is taken to exist as hydronium ion, H_3O^+. Trial moves for the ions in solution consist of random hops within a specified radius (<1 nm) of the current ion location. The energy of the trial move is calculated by summing the interactions of each ion with all other charged species within a specified cutoff distance. The validity of this cutoff approximation is ensured by choosing a large cutoff distance ($>5\kappa^{-1}$) and a large total simulation volume. Trial hops are accepted or rejected based upon the standard Metropolis criterion.[23]

The translational moves just described are responsible for establishing electrostatic equilibrium within the electrolyte and between the electrolyte and the polymer surface. Another equilibrium must also be considered: That of the acid–base reaction between the acidic polymer and the hydroxide ions in solution. This equilibrium includes the ionization of the acidic polymer

$$\mathrm{POH} \overset{K_a}{\leftrightarrow} \mathrm{PO^-} + \mathrm{H^+}, \tag{8}$$

as well as the dissociation of water

$$\mathrm{H_2O} \overset{K_w}{\leftrightarrow} \mathrm{OH^-} + \mathrm{H^+}. \tag{9}$$

Together, these are written as

$$\mathrm{POH} + \mathrm{OH^-} \overset{K_i}{\leftrightarrow} \mathrm{PO^-} + \mathrm{H_2O}. \tag{10}$$

The equilibrium constant K_i for this overall reaction is given by K_a/K_w, where K_a is the ionization constant of the acidic polymer site denoted by POH and K_w is the dissociation constant of water, approximately equal to 10^{-14} at 25 °C. These dissociation constants are used to determine the probability of a trial Monte Carlo reaction, again using the Metropolis criterion. Due to the equilibrium nature of the system, it is necessary to consider all of the individual acid–base reactions that are present. A further discussion of these equilibria is given in the Appendix.

B. Ionization of initially uncharged planar film

This Monte Carlo approach has been used to simulate the ionization of a resist surface placed in contact with developer solution. Simulation of this interfacial region begins by generating a lattice model of the resist surface. In the work presented here, a purely planar surface of polyhydroxystyrene is considered. The surface consists of a square array of 15×15 sites that represent an area of ~ 115 nm^2. It is assumed that all polymer sites are identical; that is, every polymer site

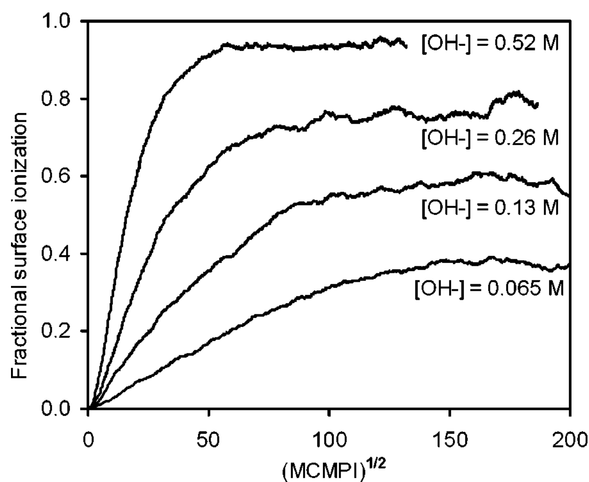

FIG. 8. Monte Carlo simulations results showing ionization of a planar surface of polymer sites with $pK_a = 10$ in contact with aqueous TMAH solutions of varying concentration.

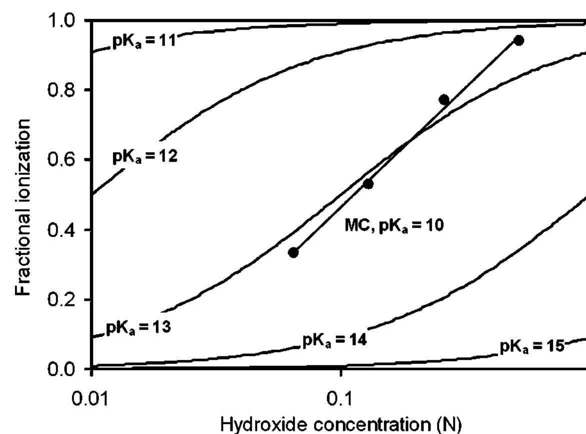

FIG. 9. Equilibrium fractional ionization of polymer: comparison of Monte Carlo results (points) with the results of Eq. (2) (curves). It is seen that Eq. (2), which does not include electrostatic effects, overestimates the ionization of the polymer.

has a pK_a of 10, independent of the ionization state of its neighbors. This approximation is valid for polyhydroxystyrene because the ionizable sites are well separated from one another. Ionization of sites that are near an already-ionized site will be influenced by the electrostatic repulsion of hydroxide from the charged site, but not by a change in the pK_a of the nearby sites.

Having generated a film surface configuration, the next step is to add the developer solution. The interfacial domain considered here consisted of the film surface plus the portion of the developer solution that was within 20 nm of the surface. The developer solution was created through sequential addition of hydroxide and tetramethylammonium ions to random locations within the space above the surface of the film until the desired bulk concentration was reached. The configuration of ions thus generated was then equilibrated for 10^3 Monte Carlo moves per ion (MCMPI) to establish electrostatic equilibrium within the solution.

Many hydroxide ions are consumed at the film surface through acid–base reaction with the polymer. To prevent this process from altering the simulated bulk concentration of hydroxide, the region of the solution between 15 and 20 nm from the surface was held at a constant concentration of hydroxide by periodically adding or removing TMAH ion pairs as needed to force the concentration in this region to match the desired bulk concentration.

Simulation of the surface ionization process was then performed until the fractional ionization of the surface stabilized. This was done for four developer concentrations in the range of 0.065–0.52 M. Dynamics of the ionization process under these four conditions is shown in Fig. 8. The fractional ionization of the film surface is plotted versus the square root of simulation time, measured in units of MCMPI. Initially, the fractional ionization increases linearly with the square root of simulation time because the hydroxide ions must diffuse to the surface. As the surface charge increases, electrostatic effects limit the diffusion process and the fractional ionization is observed to reach a steady-state value.

The steady-state fractional ionization of the surface of the film has been plotted against developer pH in Fig. 9. Also shown are the predictions of the solution equilibrium analysis [Eq. (2)] for several values of pK_a. It is clear that the solution equilibrium analysis, which does not consider electrostatic effects, overestimates the ionization of the surface. Electrostatic repulsion of hydroxide from the charged polymer surface has effectively decreased the pK_a of the polymer by approximately 3 pK_a units. Interestingly, this is approximately the change required to regenerate a reaction-limited process in our CI model.

IV. CONCLUSIONS

The effects of electrostatic interactions during dissolution of positive tone photoresists have been evaluated through the solution of the PB equation and through the Monte Carlo simulation. It has been shown that the concentration of hydroxide at the surface of the film can be much lower than the bulk concentration due to electrostatic repulsion of hydroxide ions from the negatively charged polymer surface. The degree to which the concentration of hydroxide is depleted is related to the developer concentration, which affects the equilibrium of the acid–base reaction and also influences the Debye screening length of the solution. The concentration of base at the surface of the film is also strongly influenced by the local geometry of the interface. This geometric effect is most evident on the length scale of surface roughness. When electrostatic effects are considered in conjunction with the equilibrium of the acid–base reaction, it is seen that the fractional ionization of the surface of the film is significantly decreased. Understanding the relationship between the acid–base equilibrium and electrostatic equilibrium represents an important step in our efforts to understand the fundamental dissolution mechanism of positive tone photoresists.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor Juan de Pablo at the University of Wisconsin, and to

Matthew Stone, Professor Isaac Sanchez, Professor Venkat Ganesan, and Professor Roger Bonnecaze at the University of Texas at Austin for their helpful advice. Many of the simulations presented here were performed on Pentium 4®-based machines generously donated by the Intel Corporation. This work has been supported by the SRC and DARPA. One of the authors (G.M.S.) gratefully acknowledges the Eastman Kodak Corporation for support in the form of a graduate research fellowship.

APPENDIX: MONTE CARLO TREATMENT OF ACID–BASE EQUILIBRIA

Due to the equilibrium nature of the system, it is necessary to consider all of the acid–base equilibria that are present. The following reactions are taken to be sufficient to capture the equilibrium of the system.

Ionization of polymer by hydroxide

$$\mathrm{POH}+\mathrm{OH}^- \overset{K_i}{\leftrightarrow} \mathrm{PO}^- + \mathrm{H_2O}. \tag{A1}$$

Deionization of charged polymer site with water

$$\mathrm{PO}^- + \mathrm{H_2O} \overset{1/K_i}{\leftrightarrow} \mathrm{POH}+\mathrm{OH}^-. \tag{A2}$$

Polymer autoionization

$$\mathrm{POH} \overset{K_a}{\leftrightarrow} \mathrm{PO}^- + \mathrm{H}^+. \tag{A3}$$

Deionization of charged polymer site with acid

$$\mathrm{PO}^- + \mathrm{H}^+ \overset{1/K_a}{\leftrightarrow} \mathrm{POH}. \tag{A4}$$

Dehydrolysis of water

$$\mathrm{H}^+ + \mathrm{OH}^- \overset{1/K_w}{\leftrightarrow} \mathrm{H_2O}. \tag{A5}$$

Autohydrolysis of water is neglected due to relative infrequency of the reaction.

The overall change in Gibbs free energy of each of these reactions is given by

$$\Delta G_r = -kT \ln K. \tag{A6}$$

During the Monte Carlo simulation, a trial ionization move is performed when a hydroxide ion is within a certain distance of the polymer site. This ionization distance is the distance at which the change in Gibbs free energy of the ionization of the polymer [Eq. (A3)] is equal to the unscreened Coulombic interaction between the ion and a positive point charge (proton) located at the surface of the polymer site. This methodology accounts for the removal of the proton from the polymer as given in Eq. (A3). When a hydroxide ion is within this distance, the polymer site is ionized according to the Metropolis criterion, where the energy change of the overall reaction is taken as the Gibbs energy change of Eq. (A1). This analysis results in an acceptance probability given by

$$p_{\mathrm{ACC}} = \exp(-\Delta G_{r,i}/kT) = \exp[(pK_a - pK_w)\cdot \ln 10]. \tag{A7}$$

A similar analysis is used to calculate the acceptance probability for the other individual reactions. For reactions that result in creation of an ion, an attempt is made to add that ion at a distance from the polymer site equal to the ionization distance, in a random direction. If this attempt fails due to hard sphere overlap, then the entire trial reaction move is rejected.

[1]C. A. Mack, J. Electrochem. Soc. **134**, 148 (1987).

[2]R. R. Dammel, *Diazonaphthoquinone-based Resists* (SPIE, Bellingham, WA, 1993).

[3]A. Reiser, Z. Yan, Y.-K. Han, and M. Soo Kim, J. Vac. Sci. Technol. B **18**, 1288 (2000).

[4]H. Y. Shih and A. Reiser, Macromolecules **30**, 4353 (1997).

[5]H.-Y. Shih, H. Zhuang, A. Reiser, I. Teraoka, J. Goodman, and P. M. Gallagher-Wetmore, Macromolecules **31**, 1208 (1998).

[6]K. Ueberreiter and F. Asmussen, J. Polym. Sci. **23**, 75 (1957).

[7]J. S. Papanu, D. S. Soane, A. T. Bell, and D. W. Hess, J. Appl. Polym. Sci. **38**, 859 (1989).

[8]N. Peppas, J. C. Wu, and E. D. von Meerwall, Macromolecules **27**, 5626 (1994).

[9]P. C. Tsiartas, L. W. Flanagin, C. L. Henderson, W. D. Hinsberg, I. C. Sanchez, R. T. Bonnecaze, and C. G. Willson, Macromolecules **30**, 4656 (1997).

[10]L. W. Flanagin, C. L. McAdams, W. D. Hinsberg, I. C. Sanchez, and C. G. Willson, Abstr. Pap. - Am. Chem. Soc. **218**, 112 (1999).

[11]L. W. Flanagin, Ph.D. thesis, The University of Texas at Austin, 1999.

[12]L. W. Flanagin, V. K. Singh, and C. G. Willson, J. Vac. Sci. Technol. B **17**, 1371 (1999).

[13]S. D. Burns, G. M. Schmid, L. W. Flanagin, P. C. Tsiartas, and C. G. Willson, J. Vac. Sci. Technol. B **20**, 537 (2002).

[14]G. M. Schmid, V. K. Singh, L. W. Flanagin, M. D. Stewart, S. D. Burns, and C. G. Willson, Proc. SPIE **3999**, 675 (2000).

[15]G. M. Schmid, M. D. Smith, C. A. Mack, V. K. Singh, S. D. Burns, and C. G. Willson, Proc. SPIE **4345**, 1037 (2001).

[16]G. M. Schmid, M. D. Stewart, V. K. Singh, and C. G. Willson, J. Vac. Sci. Technol. B **20**, 185 (2002).

[17]S. R. Milner, Philos. Mag. **25**, 742 (1913).

[18]W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN: The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, New York, 1992).

[19]L. W. Flanagin, V. K. Singh, and C. G. Willson, J. Polym. Sci., Part B: Polym. Phys. **37**, 2103 (1999).

[20]J. P. Valleau, L. K. Cohen, and D. N. Card, J. Chem. Phys. **72**, 5942 (1980).

[21]J. P. Valleau and L. K. Cohen, J. Chem. Phys. **72**, 5935 (1980).

[22]S. Durand-Vidal, J.-P. Simonin, and P. Turq, *Electrolytes at Interfaces* (Kluwer, Dordrecht, 2000), Vol. 1.

[23]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).