# Advancements to the critical ionization dissolution model

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The microlithographic process is dependent upon the dissolution of acidic polymers in aqueous base. The fundamental mechanism that governs the dissolution of these polymers has been the subject of considerable discussion, and a number of theories have been proposed to explain this behavior. Our research group has presented the critical ionization (CI) dissolution model to explain the dissolution of phenolic polymers in aqueous base. Specifically, the model proposes that a minimum or critical fraction of ionized sites, $f_{\text{crit}}$, on a given polymer chain must be ionized in order for that chain to dissolve. The main input parameters to this model are the critical fraction of ionized sites, $f_{\text{crit}}$, and the fraction of ionized surface sites, $\alpha$. In this work methods are established for measuring these parameters. A quantitative link between the CI model and experiment has been demonstrated for the dissolution rate and surface roughness dependence on polymer molecular weight. Methods for calculating $\alpha$ are discussed, including a new method that considers the formation of an electrostatic double layer at the resist–developer interface. [DOI: 10.1116/1.1450593]

## I. INTRODUCTION

A deeper understanding of the dissolution step of the microlithographic process will aid in photoresist synthetic design and in lithography modeling. A great deal of effort has been expended to understand the fundamental mechanism by which phenolic polymers dissolve in aqueous base. Dammel[1] and Reiser[2,3] provide a wealth of information on the topic. The dissolution of these polymers [typically novolac or polyhydroxystyrene (PHOST) resins of low molecular weight] in aqueous base has been compared to the etching of copper in nitric acid, in that a chemical reaction is required to convert the initial insoluble material (a polyol) to a soluble one (a polyion). Three primary steps are necessary for dissolution. The first is transport of hydroxide ions to the film surface. Second is the deprotonation reaction (shown in Fig. 1) in which several hydroxyl sites are ionized. The third is transport of the ionized polymer chain into the bulk of the developer.

Recently, our research group has presented the critical ionization (CI) dissolution model.[4–7] The premise of the model is that the deprotonation reaction is the key and rate limiting step in phenolic polymer dissolution. Specifically, the model proposes that a minimum fraction, $f_{\text{crit}}$, of ionizable sites, on a given polymer chain must be ionized simultaneously in order for that chain to dissolve. This model has been particularly successful in explaining the anomalous effect on film dissolution rate of adding salts to the developer solution.[4] It has also provided an explanation for the influence of polymer molecular weight on dissolution rate, as well as many other important dissolution trends.[4,5]

Modeling efforts within our group have incorporated the CI theory into a three-dimensional lattice model in which a lattice cell corresponds to an individual polymer repeat unit. The lattice simulation has been used to model film formation,[5,8] the post exposure bake[8,9] and dissolution.[4–6] The main input parameters to this model are the critical fraction of ionized sites, $f_{\text{crit}}$, and the fraction, $\alpha$, of surface sites that are ionized. The first parameter, $f_{\text{crit}}$, is a microscopic quantity. It is defined as the minimum fraction of sites on an individual polymer chain that must be ionized simultaneously in order for that polymer chain to dissolve. The second parameter, $\alpha$, is a macroscopic quantity. It is defined as the average fraction of surface sites (monomer units in contact with the developer) that remain ionized as the polymer film dissolves.

Attempts have been made to determine $f_{\text{crit}}$ experimentally, but $f_{\text{crit}}$ is a microscopic quantity and it is challenging to design an experiment that will yield an unambiguous measurement.[10] The lattice model has shown that small changes in the value of $f_{\text{crit}}$ strongly modify the response of the dissolution rate to polymer molecular weight. For a given polymer system, there is a single value of $f_{\text{crit}}$ that matches experimental dissolution rate as a function of molecular weight. Thus, it is possible to empirically fit a best value of $f_{\text{crit}}$ by comparison to a simple dissolution rate experiment.

The fraction of ionized sites, $\alpha$, can be calculated from classical equilibrium theory if the developer concentration and $pK_a$ of the polymer are known.[6] The two important factors are the equilibrium constant for the deprotonation reaction and the acidity function of the polymer. In this work, a third effect, the influence of the electrostatic repulsion of hydroxide ions by the accumulated negative charge on the dissolving polymer film (an electric double layer) is considered. Electrostatic repulsion is included in the model by solv-

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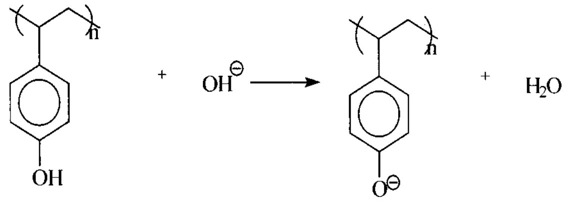


FIG. 1. Deprotonation reaction of PHOST with aqueous base.

ing the Poisson–Boltzmann (PB) equation and requires no additional input parameters. The effect is considered from both a continuum and a stochastic perspective.

One advantage of a stochastic model is that molecular size effects such as surface roughness can be predicted. For example, the observed variation of surface roughness with exposure dose[11] and molecular weight[12] are captured by the CI model.[7] Also, the induction and then rapid increase in surface roughness at the beginning of dissolution is observed in both experimental results[13,14] and the CI model.[7,13] In this work, a quantitative comparison was made between the surface roughness predicted by the CI model and that observed by AFM for PHOST films of varying molecular weight.

## II. EXPERIMENT

The polymers used in this study are highly monodisperse polyhydroxystyrene, donated from Nippon Soda. A range of molecular weights between 3000 and 15 000 were used. Films were spin cast on silicon wafers from solutions of 20% solids in propylene glycol methyl ether acetate (PGMEA) at a spin speed of 2500 rpm for 30 s. The post apply bake was 90° C for 90 s. A range of film thickness from 1 to 1.6 $\mu$m resulted. The films were dissolved in 0.11 N KOH until approximately half the film dissolved. The surface roughness was measured with a Park Scientific Instruments Autoprobe AFM. The force used was 2 nN at a scan rate of 1 Hz and a gain of 0.2. The roughness values are averages of several scans on the wafer surface.

## III. RESULTS AND DISCUSSION

### A. Determination of the critical ionization fraction $f_{\text{crit}}$

During dissolution, hydroxide ions deprotonate phenolic sites, to generate phenolate anions. The rate of this reaction is known to be very fast, so attainment of equilibrium is fast. In the CI lattice simulations, this equilibrium is very important. In our latest implementation of the model,[4–6] the first time step involves a certain fraction ($\alpha$) of the ionizable sites on the surface being deprotonated upon initial contact with the aqueous base solution. Unless a chain incorporating ionized sites dissolved (by meeting or exceeding the $f_{\text{crit}}$ criterion), these sites would remain ionized for the remainder of the simulation. However this is not entirely true, as the rate of proton transfer is high so that sites rapidly deprotonate and reprotonate and maintain a dynamic equilibrium. In the latest version of the lattice simulation, a new set of ionized monomer sites is generated in each time step, thereby mimicking the dynamic equilibrium of the deprotonation reaction. A time step is assumed to be slow enough for an entirely new equilibrium state to be reached.

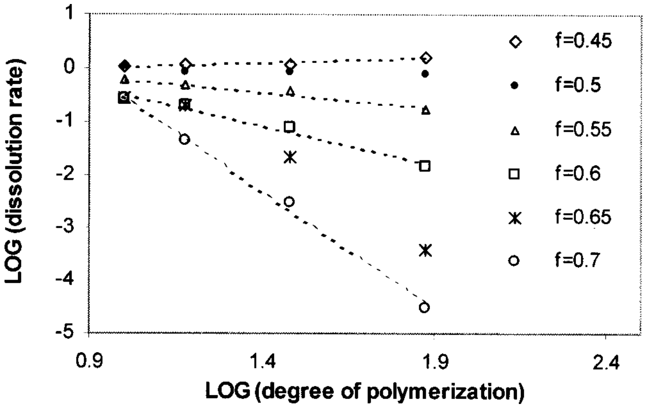


FIG. 2. Simulated response of dissolution rate as a function of degree of polymerization at various values of $f_{\text{crit}}$.

This subtle change to the CI algorithm results in several distinct changes in the simulated dissolution behavior. The deprotonation equilibrium is such that new distributions of ionization states are generated with each time step, resulting in a higher probability that some chains will meet the $f_{\text{crit}}$ criterion and dissolution will occur. For certain values of $\alpha$ and $f_{\text{crit}}$, dramatic changes in dissolution rate are observed at the surface of the film, due in part to evolution of surface roughness. This result has been proposed as an explanation for the surface rate inhibition often observed in novolac films.[7,13]

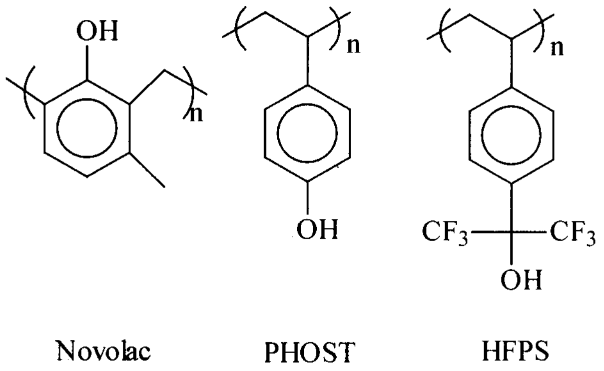
With the addition of the deprotonation reaction equilibrium, an interesting trend was observed by varying $f_{\text{crit}}$. In Fig. 2, the dissolution rate (nm/time step) is plotted against the molecular weight of the polymer chains at various values of $f_{\text{crit}}$. The lattice used was $73^3$ cells (about 50 $\text{nm}^3$), with a void fraction of 0.1, and the fraction of ionized sites ($\alpha$) was kept constant at 0.9. The lattice contained no pendant groups (blocked sites). The polydispersity was kept constant at 1.0. This condition represents monodisperse polyhydroxystyrene (PHOST).

The experimentally determined relationship between dissolution rate and molecular weight is an exponential,

$$R = \text{MW}^n, \tag{1}$$

where $R$ is the dissolution rate, MW is the molecular weight of the polymer. The exponent varies between $-0.3$ to $-3$ for a variety of novolac and PHOST fractions.[4,15–19] Our group has found that for monodisperse polyhydroxystyrene, $n \sim -2.3$.[4] A value of $f_{\text{crit}} = 0.63$ results in a slope of $\sim -2.3$.

These results indicate three significant advancements to the model. First, the molecular weight dependence of the dissolution rate can be captured quantitatively, with only one variable. (It is assumed that the fraction of ionized surface sites can be rigorously calculated, which is discussed in the next section.) This technique provides the first method for determining $f_{\text{crit}}$ for any given polymer system.



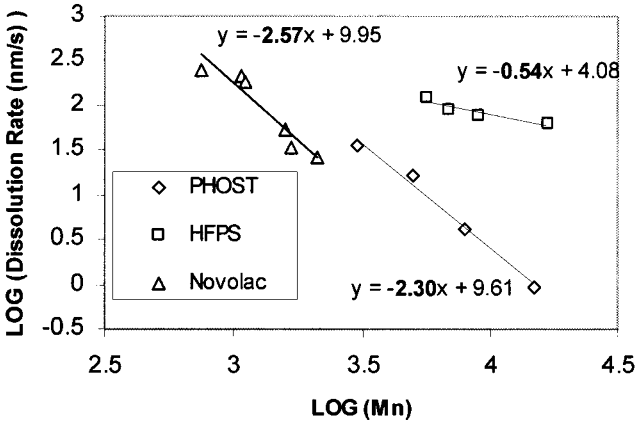


FIG. 3. Experimentally determined response of dissolution rate to changes in molecular weight for PHOST, HFPS (0.13 N TMAH), and novolac (0.12 N KOH).

Figure 3 shows the experimentally determined dissolution rate of poly($p$-hydroxystyrene), 4-bistrifluoromethylcarbinol substituted polystyrene (HFPS),[16] and novolac.[17] All three polymers show a linear change in dissolution rate with molecular weight on a log–log scale [Eq. (1)]. However, the slope of each line differs considerably. Novolac has a slope of $-2.6$, PHOST has a slope of $-2.3$, while HFPS has a slope of $-0.54$. Comparing these experimental data to the simulation as shown in Fig. 2 indicates that the best fit value of $f_{\text{crit}}$ for novolac is 0.64, for PHOST is 0.63, and for HFPS is 0.54. The molecular weight dependence of the dissolution rate of each polymer is correctly captured by the CI model by using the appropriate value of $f_{\text{crit}}$.

### B. Determining the fraction of ionized sites, $\alpha$

The previous method for determining $\alpha$ considers the equilibrium of the deprotonation reaction and the acidity function of the polymer. The equilibrium of the reaction yields an expression for $\alpha$ of the form

$$\alpha=\frac{10^{pH_o-pKa}}{1+10^{pH_o-pKa}}, \tag{2}$$

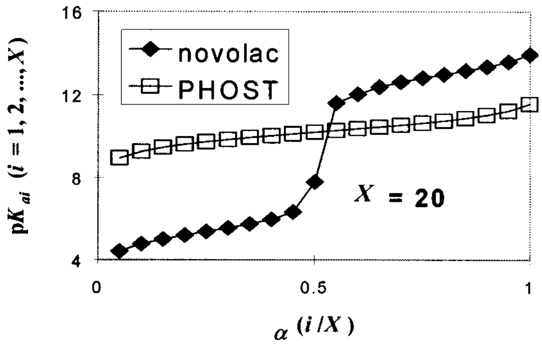


FIG. 4. Estimated $p\mathrm{K}a$ of PHOST and novolac as a function of the degree of ionization, $\alpha$.

where $pH_o$ is the $pH$ (-log of the hydrogen ion concentration) at the surface of the film, and the $p\mathrm{K}_a$ of the polymer is known. However, the $p\mathrm{K}_a$ of the polymer is also a function of $\alpha$,

$$p\mathrm{K}_a=f(\alpha). \tag{3}$$

Equation (3) defines the acidity function of the polymer, which has been estimated for both PHOST and novolac[6] based on literature data for the $p\mathrm{K}a$ of phenolic oligomers.[20,21] Figure 4 shows the estimated $p\mathrm{K}_a$ of both PHOST and novolac as a function of the degree of ionization, $\alpha$. The subtle differences in the structure of the phenolic polymers result in large differences in their acidity functions. The fraction of ionized sites ($\alpha$) was calculated by solving Eqs. (2) and (3), assuming that the hydroxide ion concentration at the surface of the film was the same as the bulk. At a developer concentration of 0.26 N, the calculated value of $\alpha$ for PHOST is greater than that for novolac (0.99 compared to 0.80), and this result is thought to explain the high dissolution rate of PHOST films compared to novolac films.[6] It is also thought to contribute to observed surface rate inhibition in novolac films.[13]

### C. Including the electric double layer

It is well known that a charged surface in contact with an electrolyte solution results in an electrostatic "double layer."[22] This is shown in Fig. 5, in which a negatively charged surface is shown in contact with a 1:1 electrolyte solution. The positive ions are attracted to the negative surface, while the negative ions are repelled. At the interface, there is a layer of negatively charged ions in close proximity to a layer of positively charged ions, hence the term "double layer."

During photoresist dissolution, the surface of the film becomes deprotonated at many sites, resulting in a net negative charge. An assumption of the critical ionization model has been that the penetration of ions within the film is negligible. That is, the polymer is thought to dissolve before significant penetration can occur. Based on that assumption, an electric double layer forms at the interface of resist and developer. The main effect of the double layer is to reduce the concentration of hydroxide ions near the surface of the resist. This

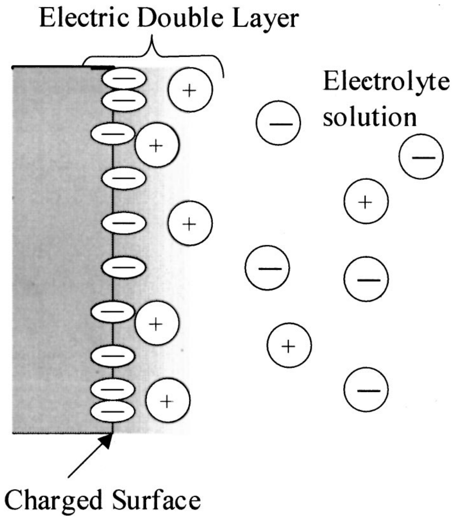


FIG. 5. Charged surface next to an electrolyte solution forms an electrostatic double layer.

in turn reduces the value of $\alpha$. The remainder of this work documents our efforts to quantify the effects of the double layer on $\alpha$.

Israelachvili provides an excellent discussion and many examples that quantify electrostatic surface charges of flat surfaces in contact with electrolyte solutions.[22] These examples were applied to a polymer film dissolving in aqueous base by a 1:1 developer solution. Here, only an abbreviated derivation of the necessary equations is presented. A complete derivation is provided elsewhere,[23] and the reader is also referred to the work of Israelachvili.[22]

The governing equation for this system is the Poisson–Boltzmann (PB) equation,

$$\frac{d^2\psi}{dx^2}=-\left(\frac{ze\rho_\infty}{\varepsilon\varepsilon_o}\right)\exp\left(\frac{-ze\psi}{kT}\right), \tag{4}$$

in which $\psi$ is the electrostatic potential, $x$ is the distance from the surface, $e$ is the charge of an electron, $z$ is the valency of the electrolyte ions, $\rho$ is the number density of ions in the bulk, $\varepsilon$ is the dielectric constant of the medium, $\varepsilon_o$ is the permittivity of free space ($8.854\times10^{-12}$ C$^2$/J m), $k$ is Boltzmann's constant, and $T$ is the temperature in Kelvin. Solving this equation yields the potential and ion concentration as a function of the distance from the film surface into the developer solution.

In order to calculate the ion concentration at the surface of the film ($x=0$), the surface charge ($\sigma$) of the film (which is directly proportional to $\alpha$) must be known. However, the ion concentration affects $\alpha$, so an initial guess must be made. First, the relationship between $\sigma$ and $\alpha$ must be determined. In the lattice simulations, the volume of a monomer unit is approximated by a cube that is 0.7 nm on a side. The corresponding area for an ionizable site is therefore 0.49 nm$^2$, with one possible electronic charge per site. Thus, for a fully ionized film surface, $\sigma$ is equal to 0.326 C/m$^2$. Therefore the relationship between surface charge, $\sigma$, and the fraction of ionized sites, $\alpha$, is

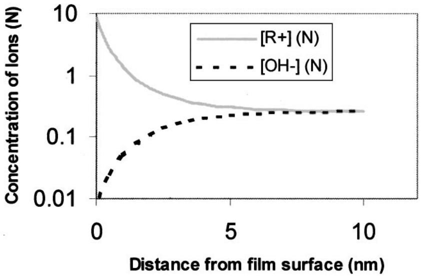


FIG. 6. Calculated concentration profile of developer ions away from the surface of a novolac film (0.26 N; $\alpha=0.55$).

$$\sigma=0.326\alpha. \tag{5}$$

The ion concentrations of a general base developer solution (ROH) away from the surface are given by the Boltzmann distribution,

$$[R^+](x)=[R^+]_\infty e^{[e\psi(x)/kT]} \tag{6}$$

$$[\mathrm{OH}^-](x)=[\mathrm{OH}^-]_\infty e^{[-e\psi(x)/kT]}. \tag{7}$$

By considering the PB equation and charge neutrality (the total charge of counterions near the surface must equal the charge on the surface), the surface potential and the surface concentration of ions can be calculated,

$$\psi_o=\frac{2kT}{e}\left[\sinh^{-1}\left(\frac{\sigma^2}{8\varepsilon\varepsilon_o kT\{[\mathrm{ROH}]_\infty+[\mathrm{AS}]_\infty\}}\right)+1\right], \tag{8}$$

$$[\mathrm{R}^+]_o=[\mathrm{R}^+]_\infty e^{(e\psi_o/kT)}, \tag{9}$$

$$[\mathrm{OH}^-]_o=[\mathrm{OH}^-]_\infty e^{(-e\psi_o/kT)}, \tag{10}$$

where the subscript "$o$" indicates the surface of the film, and [AS] is the concentration of any salts added to the developer solution. Note that the double layer analysis predicts a change in $\alpha$ (and thus dissolution rate) with added salts and with temperature. We intend to explore these relationships more carefully.

A parameter typically used to describe a double layer system is the Debye length,[22]

$$K^{-1}=\frac{0.43}{[\mathrm{ROH}]_\infty^{0.5}}, \tag{11}$$

where $K^{-1}$ is the Debye length in nm, which is the characteristic length of the electrostatic potential. Note that the Debye length is dependent only on the developer concentration, and not the surface charge or other properties of the film. In Fig. 6, the concentration profile of developer ions away from the film surface is plotted for the hypothetical case of $\alpha=0.5$, and 0.26 N developer solution.[22,23] There is a factor of 30 increase in the concentration of cations at the surface, and an identical decrease in the concentration of hydroxide ion at the surface. The Debye length is plotted against developer concentration in Fig. 7. There is a square root dependence on developer concentration. For typical lithographic applications, the Debye length is ~1 nm.

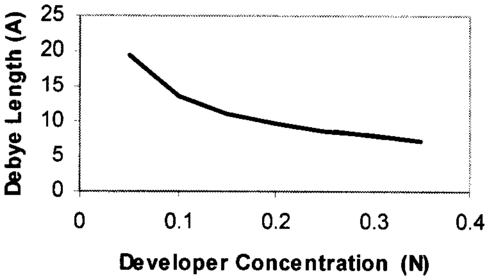


FIG. 7. Calculated Debye length as a function of developer concentration.

Equations (5), (8), and (10) can be combined into a function that relates the $p$H at the surface of the film to the $p$H in the bulk of the developer,

$$pH_o = 0.8686\left[\sinh^{-1}\left(\frac{0.0133\alpha^2}{\varepsilon\varepsilon_o kT(10^{pH_{\text{bulk}}-14}+[\text{AS}]_\infty)}\right)+1\right] \times (14 - pH_{\text{bulk}}) + 14. \qquad (12)$$

Equation (12) along with Eqs. (2) and (3) constitute a system of three equations and three unknowns that can be solved simultaneously to yield $pH_o$, $pK_a$, and $\alpha$. The solution to these equations is shown in both Figs. 8 and 9 for PHOST and novolac, respectively. The calculated value of $\alpha$ is also shown without considering electrostatic surface forces. That is, $\alpha$ was also calculated using only Eqs. (2) and (3). In each case, the calculated value of $\alpha$ drops considerably when electrostatic surface forces are considered.

There are several assumptions implicit in the above analysis. Most notably, the assumption is made that the charged surface is impenetrable to the base ions and that the surface is flat. Also, the PB equation does not consider finite ion size (steric) effects or the discreteness of surface charges. Thus far, the critical ionization model has been successful without considering diffusion of ions into the polymer matrix. The assumption has been that with typical polymers and under typical processing conditions (0.26 N TMAH), the film dissolves faster than ions can penetrate the film. For high MW phenolic polymers, Arcus has shown evidence of an interfacial region by interferometry.[24] Hinsberg *et al.* have shown evidence of an "interfacial region" for 193 nm materials by a compensated phase-locked oscillator quartz crystal microbalance (CPLO QCM) technique.[25] The gel-layer model by Reiser proposes diffusion of ions through an interfacial boundary.[2,3] In these cases, considerable diffusion of developer ions into the film can be inferred. For phenolic films, Hinsberg *et al.* have observed almost no interfacial region.[25] For low MW phenolic polymers of the sort typically used for lithographic applications, little direct experimental evidence is available to contradict the assumption of low ion penetration.

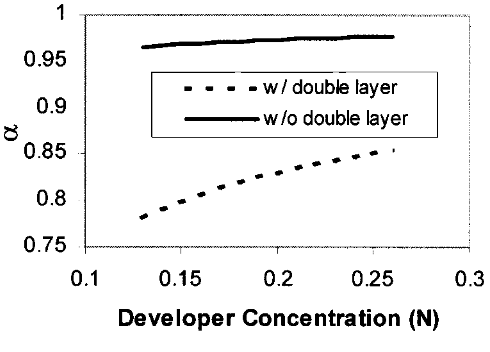


FIG. 8. Calculated fraction of ionized sites ($\alpha$) for a PHOST film at various developer concentrations with and without considering the double layer effect.

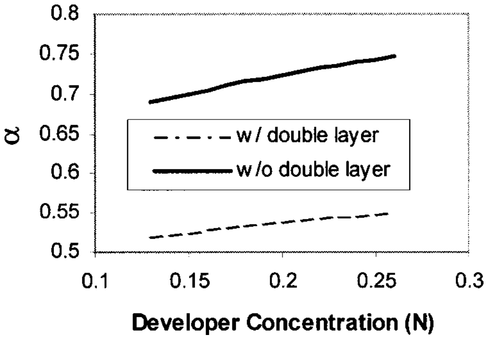


FIG. 9. Calculated fraction of ionized sites ($\alpha$) for a novolac film at various developer concentrations with and without considering the double layer effect.

The assumption of a flat surface is another important issue. At high degrees of polymerization (dp=75), the surface roughness during development is on the order of 5 nm (Fig. 12), and the Debye length is on the order of 1 nm. For such cases, the assumption of a flat surface is no longer valid. However, neither of these assumptions is necessary if the double layer is considered from a stochastic point of view. An added benefit of a stochastic approach is that finite ion size effects can be investigated. A simple technique has been used to incorporate this effect directly into the CI lattice simulations.

## D. A stochastic approach to the double layer

The method used thus far for incorporating the double layer effect into the lattice simulations is shown in Fig. 10. As a site becomes ionized, an adjacent site is chosen at random and filled with the positive counterion (+). The double layer then exists as discrete positive charges directly adjacent to ionized sites. (This layer is more accurately described as the Stern layer, which defines the immobile ions in direct contact with the ionized surface. Note that the following analysis assumes a monovalent developer cation.) One effect of adding the countercation is to block ionization of adjacent sites. The overall effect is to lower the fraction of ionized surface sites (just as the continuum model predicts). In Fig. 10(b), the size of the counterion is assumed to be identical to the size of the monomer repeat unit. However, the size of the cation can vary considerably.

A probabilistic approach has been taken to account for ions of varying size. For a given cation site, the volume of the cation (not the site) is used to calculate a probability that the developer site may ionize another adjacent polymer site.

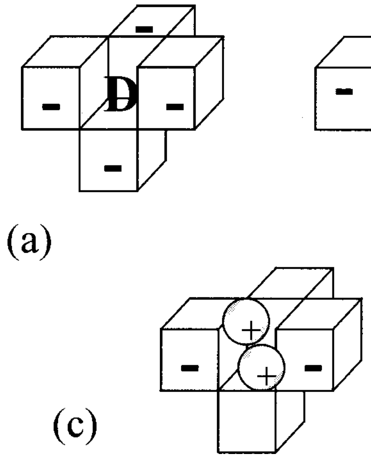


FIG. 10. Implementation of the stochastic double layer. (a) No double layer: a developer site is capable of ionizing five adjacent sites; (b) $P_{\mathrm{cation}}=1.0$: a developer site is capable of ionizing only 1 adjacent site; (c) $P_{\mathrm{cation}}=0.5$: a developer site is capable of ionizing two adjacent sites.

For example, if the cation is half the size of a monomer site, then the probability, $P_{\mathrm{cation}}$, that the site may ionize another adjacent site is 0.5. Simply stated,

$$P_{\mathrm{cation}}=\frac{V_{\mathrm{cation}}}{V_{\mathrm{monomersite}}}. \tag{13}$$

A random number is generated in each case, and if the random number is greater than $P_{\mathrm{cation}}$, another adjacent site is ionized. In other words, if a monomer site is twice the size of a cation, a single developer site is capable of housing two cations [Fig. 10(c)]. This approach is practical if the cation size is less than the size of the monomer unit. For typical applications, this is always true unless the developer consists of tetraethylammonium or a larger cation. Figure 11 demonstrates the decrease in dissolution rate with increasing cation size.

The predicted decrease in dissolution rate with increasing counterion size agrees with experimental observations.[9] Intuitively, larger ions will penetrate the film slower than small ions, so it has been proposed that the dissolution rate is related to the penetration time of the ions. However, the double layer stochastic analysis predicts a decrease in dissolution rate with increasing ion size without any penetration of the counterion into the film.

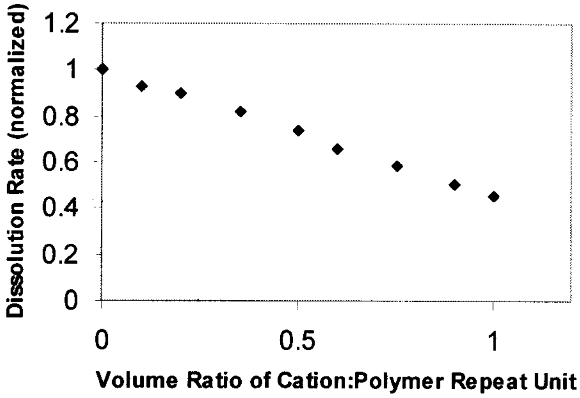


FIG. 11. Change in simulated dissolution rate with size of the developer counterion.

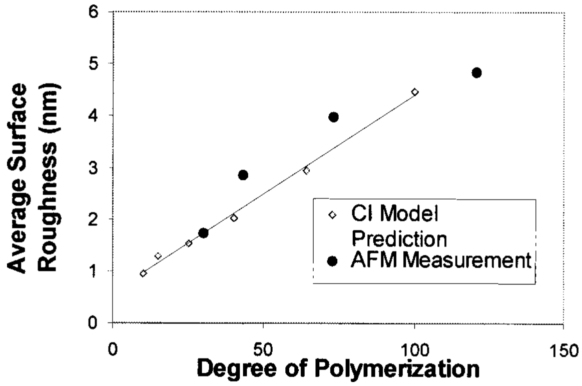


FIG. 12. Average surface roughness as a function of degree of polymerization for PHOST determined by the CI lattice model and by AFM.

### E. Surface roughness

The algorithm used by the CI model to calculate surface roughness has been previously discussed.[7] The surface roughness was calculated for the same simulations used in Fig. 2. Figure 12 shows the average surface roughness plotted against degree of polymerization, determined by simulation and experiment. The surface roughness was found to increase linearly with increasing molecular weight, which is consistent with the results reported by Yoshimura *et al.*[12] There is good agreement between the CI model prediction of surface roughness and the experimentally observed roughness over a MW range of 3 000–15 000.

## IV. CONCLUSIONS

Several advancements to the CI model have been presented. A method has been described that allows determination of $f_{\mathrm{crit}}$ and a quantitative prediction of the molecular weight dependence on dissolution rate has been presented. The electric double layer has been included in the model. This effect has a very significant impact on calculating the fraction of ionized surface sites, $\alpha$. A simple stochastic representation of the double layer predicts a decrease in dissolution rate with increasing ion size. A satisfying, quantitative agreement between measured surface roughness and the prediction of the CI lattice model were found for a range of polymer molecular weights.

## ACKNOWLEDGMENTS

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