Polymer Dissolution Model:
An Energy Adaptation of the Critical Ionization Theory

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ABSTRACT

The current scale of features size in the microelectronics industry has reached the point where molecular level interactions affect process fidelity and produce excursions from the continuum world like line edge roughness (LER). Here we present a 3D molecular level model based on the adaptation of the critical ionization (CI) theory using a fundamental interaction energy approach. The model asserts that it is the favorable interaction between the ionized part of the polymer and the developer solution which renders the polymer soluble. Dynamic Monte Carlo methods were used in the current model to study the polymer dissolution phenomenon. The surface ionization was captured by employing an electric double layer at the interface, and polymer motion was simulated using the Metropolis algorithm. The approximated interaction parameters, for different species in the system, were obtained experimentally and used to calibrate the simulated dissolution rate response to polymer molecular weight and developer concentration. The predicted response is in good agreement with experimental dissolution rate data. The simulation results support the premise of the CI theory and provide an insight into the CI model from a new prospective. This model may provide a means to study the contribution of development to LER and other related defects based on molecular level interactions between distinct components in the polymer and the developer.

Keywords: Critical Ionization model, Photoresist Dissolution, Mesoscale modeling

1. INTRODUCTION

The semiconductor industry has maintained the pace of Moore's Law for nearly 40 years, and one of the main contributors has been advancement in the field of lithography [1]. However, the technical challenges ahead are severe, and the future roadmap laid by the International Technology Roadmap for Semiconductors looks very red (i.e. no solution has been found for a specific problem) [2]. Control of LER is becoming a key driver for lithographic processes, and shrinking CDs (critical dimension, usually the dimension of the smallest feature) will only magnify the problem. The current CDs are such that even a single polymer molecule can have a considerable impact on LER. Therefore, a molecular level understanding of each process is required. Slow progress has been made in improving LER based on pure empiricism, but there is little fundamental understanding of the origin of LER to guide process and material changes directed towards improvement. Computer simulations are a cost-effective approach to exploring the huge process space. Currently available simulators are based on continuum model approximations and are therefore fast but incapable of predicting stochastic phenomenon like LER, variance in photoresist dissolution, etc. Mesoscale modeling is one promising approach to capture the stochastic phenomena at the molecular level within a reasonable computational time [3].

It was proposed earlier that low frequency LER is the result of chemical amplification in the photoresist with non-uniform distribution of acid [4]. We also believe that the same phenomenon makes particles coalesce in the developer to form larger aggregations of insoluble material that ultimately deposit on the wafer surface and the tooling. The final LER and the related defects are the combined effect of predevelopment and development steps. Our group has developed a mesoscale model to simulate spin coating, post apply bake (PAB), exposure and post exposure bake (PEB)

[3, 4]. Next, we attempt to improve our understanding of the photoresist dissolution phenomena and efficiently explore the statistical excursions that lead to LER and the formation of insoluble residues. Our goal is to achieve quantification of the effect of changes in resist composition, developer concentration, and process variables on LER and the resultant defectivity.

In the past, several models have been proposed to explain the dissolution of phenolic polymers in aqueous base. Using a membrane model, Arcus proposed that the transport of base through a gel layer is the rate determining step for dissolution [5]. Reiser and co-workers used the percolation model, which emphasizes the propagation of base through a penetration zone between the developer and the polymer resin as the rate limiting step [6]. The critical ionization (CI) model states that in order for a polymer chain to dissolve, some critical fraction of its acidic sites must be ionized by basic developer solution [7, 8]. The main input parameter used is the critical fraction of chain acidic sites, f_{crit}, which must be ionized to enable dissolution. The model has given a satisfying explanation for various experimental observations, including, the inverse relation of dissolution rate with the logarithm of molecular weight of polymer; nearly zero dissolution rate below a critical, non-zero base concentration; increase in surface roughness with higher molecular weight of the polymer; etc. Although the qualitative trends can be obtained, quantitative assessment requires an unambiguous estimate of f_{crit}. This in turn demands a basic understanding of the origin of f_{crit} and its variation, if any, with the process variables such as developer concentration, molecular weight of the polymer, and degree of chemical blocking of polymer.

The current model attempts to take a more fundamental energy approach to dissolution based on the interactions between different species in the polymer and the developer. Like the CI model, this model also does not account for base diffusion through a "penetration zone". It assumes that base is readily available for deprotonation at polymer phenolic sites. The model inputs are the interaction parameters, which are obtained using interfacial energy measurements. Similar to f_{crit} in CI model, the current model relies on a favorable interaction between the ionized part of the polymer and the developer solution to render the polymer soluble. Mesoscale modeling using this approach not only allows us to account for the ionized part (favorable interaction with developer) but also takes into account the chain configuration by considering the interactions of the non-ionized part of the chain with the developer and the polymer film. Throughout the paper, polymer refers to poly(p-hydroxystyrene) (PHS) and developer refers to the aqueous base solution of tetra-methyl-ammonium hydroxide (TMAH). If mentioned, the chemical blocking group refers to the t-butyloxycarbonyloxy (tBOC) group.

2. MESOSCALE POLYMER DISSOLUTION MODEL

2.1 System Configuration

First, a 3D cubic lattice structure is created to simulate the poly(p-hydroxystyrene) film. Each cell in the lattice is assigned either as monomer (where a string of connected monomer cells represents a polymer chain) or as void. A completely random configuration is obtained using a Monte Carlo approach considering periodicity in the x and y direction. The next step involves densification of the lattice by reducing the void fraction [9]. The developer film, treated with the continuum model, is then added to the lattice structure with lattice grids extended into the developer film. The resultant lattice is the starting input configuration for the dissolution step. Next, we consider the steps involved in polymer dissolution, namely, surface ionization and polymer dynamics (motion and solvation). Fig. 1 illustrates the lattice configurations described above.
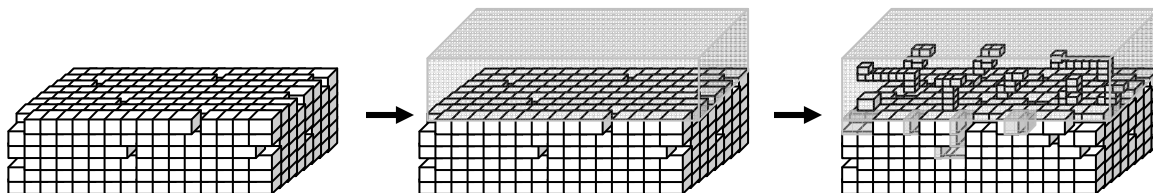

Figure 1. Lattice configurations at different stages of mesoscale simulation.

2.2 Surface Ionization

When an aqueous base (developer) comes in contact with the phenolic polymer, deprotonation of the ionizable acidic sites accumulates a negative charge at the polymer-developer interface. The charged surface results in the depletion of hydroxide ions near the interface, and an electric double layer is formed. The Poisson-Boltzmann (PB) equation can be solved to yield the ion concentration at the charged surface. The following equilibrium reactions and equations are considered to capture the surface ionization phenomenon [10-12]:

$$POH + OH^- \Leftrightarrow PO^- + H_2O ,$$
$$(1-\alpha) \qquad\qquad \alpha$$

(1)

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

(2)

$$[OH^-]_o = [OH^-]_{bulk} . e^{\left[e_c \psi_o / k_B T \right]} ,$$

(3)

$$\psi_o = \frac{2k_B T}{e_c} \sinh^{-1}\left(\frac{\sigma}{0.117\sqrt{[ROH]}} \right) ,$$

(4)

$$\sigma = -0.326\alpha,$$

(5)

where POH represents the polymer phenolic site; α is the fractional surface ionization; pH_o is the pH at the surface; pKa is the negative logarithm of dissociation constant for deprotonation reaction; $[OH^-]_o$ and $[OH^-]_{bulk}$ are the hydroxide ion concentrations at the surface and in the bulk; ψ_o is the electrostatic potential at the surface in V; σ is the surface charge density in C/m^2; [ROH] is the concentration of an aqueous base in M; and e_c is the charge of an electron. Eq. (5) is derived based on lattice grid length of 0.7 nm [11]. Eqs. (2) – (5) can be solved simultaneously to get the fractional surface ionization as a function of developer concentration. Throughout the simulation, the value of pKa used is 10.25, same as that for homogenous solution [13]. Fig. 2 shows the fractional surface ionization for different values of base concentration at equilibrium condition. Here, the polymer-developer interface is assumed to be at equilibrium at all times during the dissolution step. In reality, new non-ionized sites are exposed as the polymer dissolves. The relative magnitude of the kinetic parameters (for deprotonation reaction) and dissolution rate determine the shift from equilibrium. Dynamic equilibrium is maintained in the model by considering ionization/deionization steps at the polymer-developer interface. Ionized or deionized monomer cells are selected randomly at the interface with selection probability α or (1-α), respectively. The selected cell is then deioned or ionized with probability (1-α) or α, respectively, resulting in the same probability for the ionization or deionization step at equilibrium.
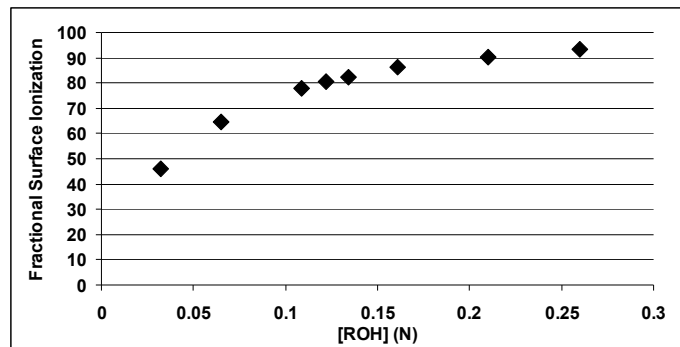

Figure 2. Fractional surface ionization for different values of base concentrations.

2.3 Polymer Dynamics

The ionization of phenolic sites lowers the interaction energy between the polymer chain and the developer resulting in an attractive force for polymer dissolution. As the polymer chains on the surface move, the developer penetrates further into the polymer film and ionizes the chains beneath the top layer. Here, the developer is treated with a continuum approximation, and the possible effects of diffusion are ignored. A system of moves for lattice polymers, as described by Verdier and Stockmayer, are used to simulate the polymer dynamics at the polymer-developer interface [9, 14]. The change in energy of the system is calculated before and after the randomly generated proposed move. In addition to excluded volume restrictions, the move is then accepted or rejected using Metropolis algorithm

$$A_{mn} = \begin{cases} e^{-(E_n - E_m)/kT} & if \ (E_n - E_m) > 0 \\ 1 & otherwise, \end{cases} \tag{6}$$

where A_{mn} is the acceptance probability for a move from a state with energy E_m to state with energy E_n. Eq. (6) implies that moves which are energetically favorable (negative energy change) are always accepted while ones which are energetically unfavorable are accepted with a small but finite probability. The interactions with only the nearest neighbors (approximated with interfacial energy) are considered while evaluating the energy change for any transition in the system. This requires an estimate of the interfacial energies between the different species in the system.

The CI model used f_{crit} as the criteria for chain solvation. The present model employs the Metropolis algorithm based on the energy change during the solvation of the chain. The change in energy is evaluated by comparing the system energy when the chain is attached to the polymer film (partially dangling) to the case in which it is fully dissolved into the developer. This energy change can be viewed as the combined effect of energy change due to the ionized part and the unionized part of the chain, i.e.

$$\Delta E_{chain\,solvation} = \underset{(-ve)}{\Delta E_{ionized\,part}} + \underset{(+ve)}{\Delta E_{unionized\,part}} \tag{7}$$

It is the favorable interaction between the developer and the ionized part of the chain that lowers the system energy during the chain solvation step. On the other hand, the unfavorable interaction between the unionized part (exposed to the developer or embedded into the polymer film) increases the system energy and thus opposes the chain solvation. In addition, the chain configuration influences the energy change. For example, an unionized cell may have all four neighbors as polymer or as developer or combinations of both, etc. Thus, using the Metropolis algorithm for chain solvation, we can account for the chain ionization, the chain configuration, and the stochastic behavior during the polymer dissolution.

As described above, the major steps involved in the model are surface ionization (ionization/deionization), polymer motion, and polymer solvation. The assumption of equilibrium at the polymer-developer interface is satisfied by including enough ionization/deionization steps before any polymer motion or polymer solvation step. This ensures that the fractional surface ionization (α) maintains a constant equilibrium value at all times.

3.   PARAMETER ESTIMATION

In the present model, the evaluation of a change in system energy requires the knowledge of the interfacial energies between different species including unionized poly(p-hydroxystyrene) (PHS), ionized poly(p-hydroxystyrene) (iPHS), protected poly(p-hydroxystyrene) (PHStBOC), developer (TMAH), and void. Here we describe different techniques used to estimate these parameters.

The surface energy of a solid surface can be estimated using a thermodynamic model proposed by van Oss, Good, and Chaudhury that includes dispersion (γ^{LW}), Lewis acid (γ^{p+}) and Lewis base (γ^{p-}) components (Eqs. (8) and (9)). These components are obtained by measuring the contact angles of the solid surface with three sample liquids (water, diiodomethane and glycerol) [15, 16]. Interfacial energy between two solid surfaces can also be estimated using Eq. (8), once all the three components are known for both the solids. The surface tension of a liquid can be measured by pendant

drop experiments. The interfacial energy between the solid and the liquid is calculated by measuring the contact angle of the solid surface with the liquid and then using the Young-Dupre equation (Eq. (10)).

$$\gamma_{12} = \left(\sqrt{\gamma_{1V}^{LW}} - \sqrt{\gamma_{2V}^{LW}} \right)^2 + 2\left(\sqrt{\gamma_{1V}^{p+} \cdot \gamma_{1V}^{p-}} + \sqrt{\gamma_{2V}^{p+} \cdot \gamma_{2V}^{p-}} - \sqrt{\gamma_{1V}^{p+} \cdot \gamma_{2V}^{p-}} - \sqrt{\gamma_{1V}^{p-} \cdot \gamma_{2V}^{p+}} \right) \tag{8}$$

$$\gamma_{1V} = \gamma_{1V}^{LW} + 2\sqrt{\gamma_{1V}^{p+} \cdot \gamma_{1V}^{p-}} \tag{9}$$

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos\theta \qquad \text{(Young-Dupre Equation)} \tag{10}$$

The following scheme was used to estimate the particular interaction parameters:

- PHS – PHS, PHStBOC – PHStBOC, TMAH – TMAH, Void – Void:
  No interaction energy within similar uncharged species.
- PHS – Void, PHStBOC – Void:
  The thermodynamic model was used to get the surface energy of PHS and PHStBOC. Contact angle measurements were done on coated films of PHS and 100% protected PHS (PHStBOC).
- PHS – PHStBOC:
  The thermodynamic model using the model components obtained for PHS and PHStBOC
- iPHS – Void, iPHS – PHS, iPHS – PHStBOC:
  The interaction parameters of iPHS with uncharged neighbors are approximated with PHS parameters i.e. PHS – Void, PHS – PHS, PHS – PHStBOC, respectively.
- TMAH – Void:
  Pendant drop experiments at different developer concentrations.
- PHS – TMAH, PHStBOC – TMAH:
  The Young-Dupre equation was used to get the interfacial energy by measuring the contact angles of TMAH with PHS and PHStBOC films at different developer concentrations. To avoid any charging at the surface, TMACl was used instead of TMAH for PHS – TMAH contact angle measurements. Fig. 3 shows the interfacial energies of TMAH with PHS and PHStBOC at different developer concentrations. Results indicate that interaction energies do not depend strongly on the developer concentration and are therefore considered constant for the model with the value evaluated with respect to water (zero developer concentration).
- iPHS – iPHS:
  From Columbic interactions between the ions in addition to van der Waals interactions
- iPHS – TMAH:
  Dissolution of charged PHS (iPHS) in TMAH makes it difficult to accurately measure the contact angles. Instead, this interaction is considered as a model parameter (ξ) and estimated by fitting experimental data at different developer concentrations.
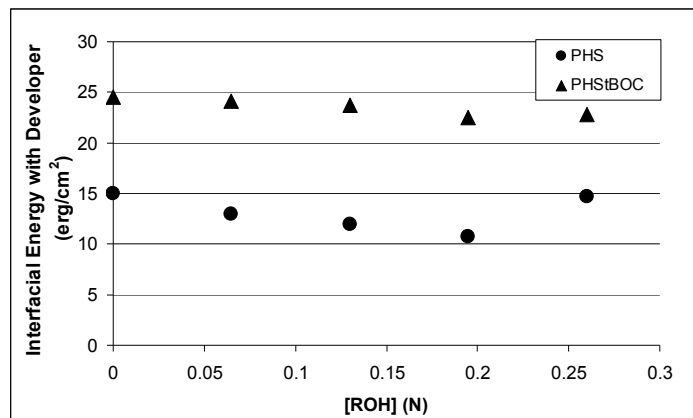

Figure 3. Interfacial energy of polymer and developer at various developer concentrations.

This parameter may also be estimated theoretically using electrowetting theory with simplifying assumptions [17]:

$$\gamma_{sl}^{eff} = \gamma_{sl} - \frac{d_H}{2\varepsilon_o\varepsilon_l}\sigma^2 = \gamma_{sl} - \frac{d_H}{18.82\varepsilon_o\varepsilon_l}\alpha^2 \qquad (11)$$

where γ_{sl} is the solid-liquid interfacial energy (PHS – TMAH), γ_{sl}^{eff} is the effective interfacial energy (iPHS – TMAH) with electric double layer at the solid-liquid interface, ε_l is the dielectric constant of the liquid and d_H is the distance from the surface to where all counter-ions are assumed to be located (Helmholtz model).

Calibration scheme: Fig. 4 exhibits the calibration scheme used in the current model. The simulated dissolution rate response to polymer molecular weight was calibrated with the experimental response by varying the model parameter, ξ (iPHS – TMAH). Each trial corresponds to different time conversion factor, Γ. To get the relation between the simulated and the real time scale, Γ was obtained by pivoting the simulated curve at one point (point A in Fig. 4) on the experimental response curve. Thus the best fit curve yields the model parameter, ξ, and the time conversion factor, Γ, at a specific developer concentration. Once Γ is known, ξ can be obtained as a function of developer concentration by matching experimental dissolution rates with simulated dissolution rates for any polymer molecular weight. Noting that the total number of Monte Carlo steps (MCS) scales with the surface area of the polymer film (L^2), the real time can be estimated as follows:

$$Real\ Time = \left(\frac{MCS}{L^2}\right).\Gamma \qquad (12)$$
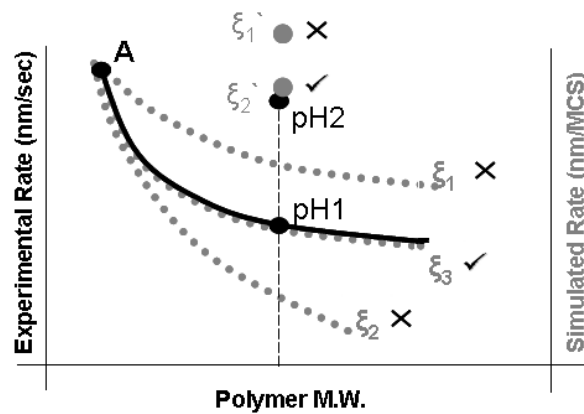

Figure 4. Calibration Scheme for Dissolution Rate Response.

Table 1 exhibits an energy matrix (normalized with thermal energy, $k_B T$) obtained as described above. Every parameter other than the iPHS – TMAH interaction parameter (ξ) is considered independent of developer concentration. The calibration gives ξ at different developer concentrations and the results are described in next section. It is imperative to note that interaction parameters for bulk polymers (PHS – PHS, PHS – PHStBOC, PHStBOC – PHStBOC) are lower than the polymer interaction parameters with developer (TMAH – PHS, TMAH – PHStBOC). This means it is energetically unfavorable for the polymer to move from the bulk into the developer. As shown later, it is the lower interaction parameter between the ionized part of the chain and the developer (TMAH – iPHS) which makes polymer solvation energetically favorable.

	PHS	PHStBOC	TMAH	iPHS	Void
PHS	0	0.26	1.79	0	5.86
PHStBOC	0.26	0	2.92	0.26	3.97
TMAH	1.79	2.92	0	ξ	8.67
iPHS	0	0.26	ξ	1	5.86
Void	5.86	3.97	8.67	5.86	0

Table 1. Interaction parameter (normalized with thermal energy, $k_B T$) matrix for different species in the system.

4. RESULTS AND DISCUSSIONS

4.1 Simulated Dissolution Rate Response

Fig. 5 shows a comparison between the experimental and the simulated dissolution rate response to the polymer (PHS) molecular weight at various developer (TMAH) concentrations. Most of the experimental data were obtained from the previous study on dissolution rate by Tsiartas *et al* [7]. Additional experiments were performed to measure the rates at higher developer concentration (0.21 N and 0.26 N). The simulated response to the polymer molecular weight was fitted to the experimental response at 0.134 N developer concentration to obtain the model parameter, ξ, at that concentration. Then ξ was evaluated at different developer concentrations by matching the simulated rate with experimental rate at polymer molecular weight ~ 9700. Simulated responses at 0.109 N, 0.122 N and 0.161 N developer concentrations show good agreement with the experimental data. Fig. 5 also shows the predicted dissolution rate responses at 0.21 N and 0.26 N developer concentrations. Currently, efforts are underway to simulate the dissolution rate response for polymer with the same molecular weight but different levels of chemically blocking.
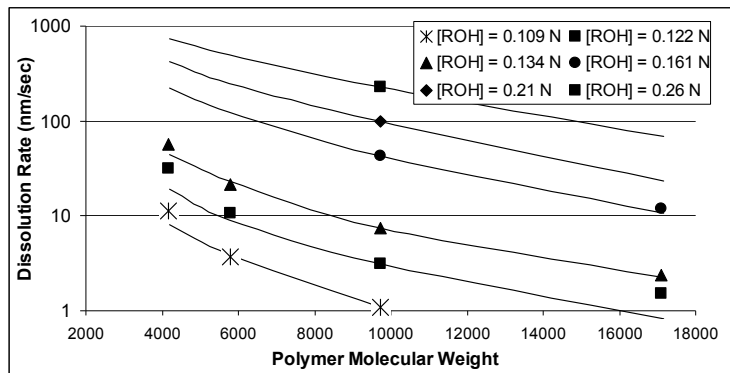

Figure 5. The experimental (dots) and the simulated (lines) dissolution rate response.

Fig. 6 shows the variation of the iPHS – TMAH interaction parameter (model parameter, ξ) as a function of developer concentration. The calibration results show that the interaction energy decreases (more favorable for polymer solvation) with an increase in developer concentration. The same trend is expected using Eq. (11) based on the electrowetting theory. This result suggests qualitative agreement with experimental observations.

- *No dissolution at non-zero critical base strength*: As shown in Fig. 3 the interaction energy of the polymer with the developer at zero developer concentration (i.e. water) is positive i.e. the polymer prefers to be in the bulk when compared to developer solution. While the interaction energy of ionized polymer with the developer in the range of concentration shown in Fig. 6 is negative i.e. the polymer prefers to be in developer when compared to the bulk. At some intermediate, finite developer concentration, the interaction energy would be zero implying the same affinity of the polymer towards the bulk and the developer solution. Around this point dissolution rate approaches zero. From Eq. (11) this point would occur when

$$\gamma_{sl} \approx \frac{d_H}{18.82\varepsilon_o\varepsilon_l}\alpha^2 \quad \Rightarrow \gamma_{sl}^{eff} \to 0 \tag{13}$$

- *High dissolution rate sensitivity to the developer concentration*: An increase in developer concentration not only increases the fractional surface ionization (see Fig. 2) but also reduces the interaction energy between the ionized polymer and the developer resulting in high dissolution rate sensitivity to the developer concentration. It also explains the finite dissolution rate of polymer even with a high degree of chemical blocking at high developer concentration. Although the number of ionizable sites is lowered with chemical blocking, the more favorable interaction between the ionized part of the polymer and the developer at high developer concentration results in polymer dissolution.
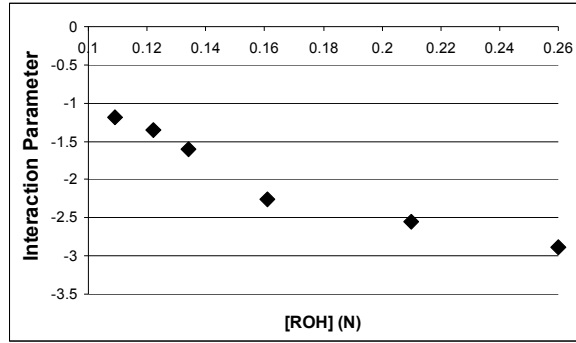
Figure 6. Fitted interaction parameter (normalized with thermal energy, $k_B T$) between the ionized PHS and the developer at different developer concentrations.

4.2 Solvated Chain Configuration

Fig. 7 shows the simulated results for progression of a single chain during the dissolution step. The three curves represent the fraction of the chain that is ionized, F; fraction of the chain that is in contact with the polymer (embedded into the polymer film or on the surface), P; and the normalized energy change required to solvate the chain at that instant. The fraction 'P' for any chain is based on the fraction of polymer chain neighbors (excluding itself) to the maximum number of neighbors possible (4 x degree of polymerization). Initially, the chain is not ionized (F = 0) and completely embedded into the polymer film ($0 < P \leq 1$), which means the required energy change is high and therefore unfavorable for chain dissolution. As time progresses, the deprotonation of acidic sites increases the number of ionized sites on the polymer chain. This increase in fraction F favors the polymer-developer interaction which further leads to a higher fraction of the chain exposed to the developer for more ionization. Due to the increase in F and reduction in P, the required energy change for the chain solvation reduces to an extent that chain dissolution becomes energetically favorable. Eventually, the chain is solvated and removed from the polymer film.
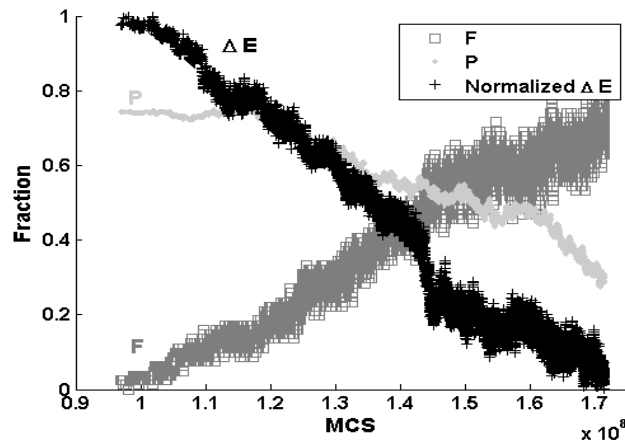

Figure 7. Progression of F, P and normalized energy change for a single change with Monte Carlo Steps (developer concentration: 0.134 N, polymer molecular weight ~ 9700).

Fig. 8(a) shows the distribution of energy change during chain dissolution. One can see that the major fraction of chains dissolve when chain solvation is energetically favorable (energy change is negative). The use of the Metropolis algorithm for chain solvation also allows a small fraction of chains to dissolve with small but positive energy change. Fig. 8(b) shows the distribution of the fraction of the chain that is ionized, *f*; and the fraction of chain in contact with the polymer film, *p*, at the time of dissolution. The distribution of *f* obtained is consistent with the simple CI model i.e. there exists a critical fraction (distribution around mean *f* for the current model) which should be ionized for chain solvation. It is worthy to note that the distributions shown in Fig. 8 depend on the time scale of polymer chain solvation step. In the current model it was assumed to be the same as time scale for polymer motion.
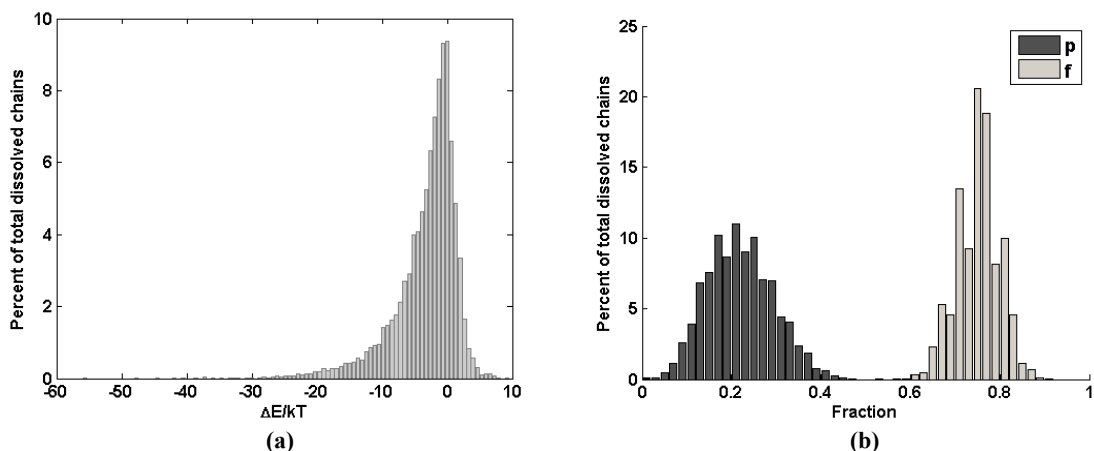
Figure 8. (a) Distribution of energy change, (b) *f* and *p* at the time of chain solvation (developer concentration: 0.134 N, polymer molecular weight ~ 9700).
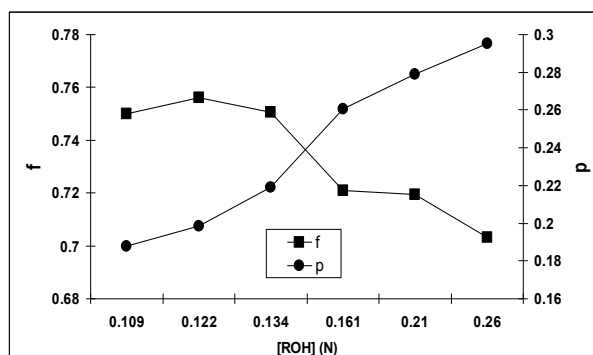

Figure 9. The variation in the mean values of *f* and *p* distributions with change in developer concentration.

Fig. 9 shows the variation in the mean values of *f* and *p* distributions with change in developer concentration. The mean *f* increases with a decrease in the developer concentration, i.e. it takes a higher ionized fraction of a chain at a lower developer concentration to render the chain soluble (due to lesser favorable interaction at lower developer concentration). A similar argument holds for a decrease in mean *p* with a decrease in the developer concentartion, which implies a higher fraction of the chain should be exposed to the developer before it is dissolved. No considerable change has been observed in mean value of *f* with changes in molecular weight of the polymer ranging from ~4000 to ~17000.

4.3 Developer Penetration

Fig. 10 shows the progression of the developer volume fraction in the polymer-developer system. The volume fraction of the developer is plotted against the normal z direction at different thicknesses of the developed film. The developer penetration depth (finite thickness for polymer-developer interface with dangling chains) remains almost constant as time progresses. Fig. 11 shows the developer penetration depth at different developer concentrations and polymer molecular weight. Higher molecular weight polymers have longer dangling chains at the polymer-developer interface, which manifests as higher penetration depths. An increase in the developer concentration means a favorable interaction between the polymer and the developer. Therefore, solvation occurs at slightly higher *p* (lesser fraction of a chain is exposed to the developer) and hence the lower penetration depth.
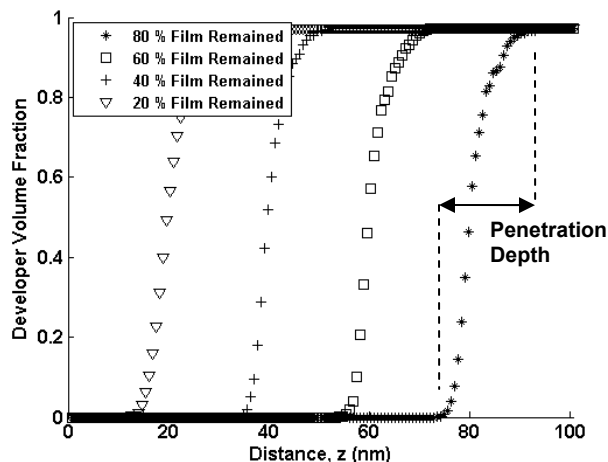
Figure 10. Progression of developer profile at various developed film thickness (developer concentration: 0.134 N, polymer molecular weight ~ 9700).
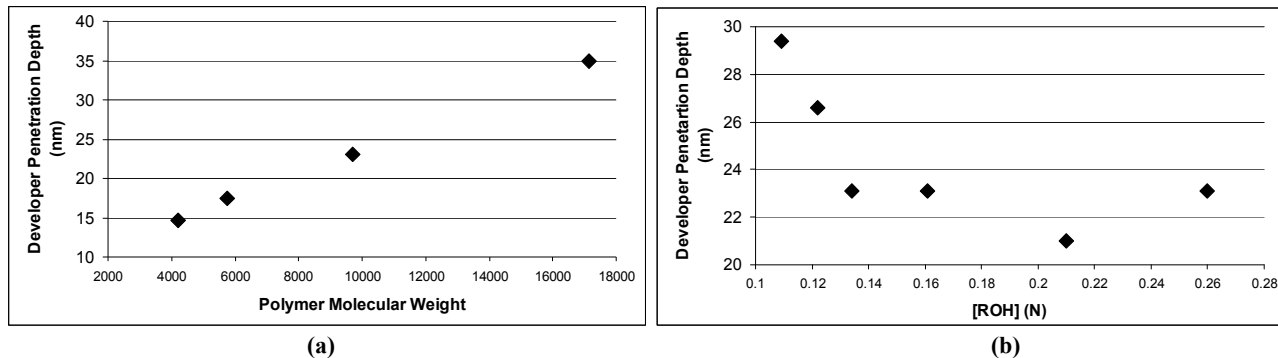

(a)	**(b)**

Figure 11. Developer penetration depth at different (a) polymer molecular weight (0.134 N developer concentration) and (b) developer concentration (polymer molecular weight ~ 9700).

5. CONCLUSIONS

A three-dimensional, molecular level polymer dissolution model has been developed. The model is based on an adaptation of critical ionization theory using a fundamental energy analysis approach. The surface ionization is considered using an electric double layer theory while the polymer dynamics at the polymer-developer interface are captured by considering the interactions of the nearest neighbors. Interaction energy parameters between different species in the polymer-developer system were determined experimentally. The model was calibrated for dissolution rate response to the polymer molecular weight and developer concentrations. The predicted response is in good agreement with experimental dissolution rate data. Results obtained from mesoscale simulations using the energy approach support the premise of the critical ionization theory. Currently, efforts are underway to study the contribution of development to LER and other related defects.

ACKNOWLEDGEMENTS

REFERENCES

1. Moore, G.E., Electronics, 1965. **38**.
2. *International Technology Roadmap for Semiconductors (ITRS) official website.*
3. Schmid, G.M., et al., "*Recent advances in a molecular level lithography simulation,*" Proc. SPIE-Int. Soc. Opt. Eng., 2000. **3999**(Pt. 2, Advances in Resist Technology and Processing XVII): p. 675-685.
4. Meiring, J.E., et al., "*Using Mesoscale Simulation to Explore Photoresist Line Edge Roughness,*" Proceedings of SPIE, 2005. **5753**.
5. Arcus, R.A., "*A membrane model for positive photoresist development,*" Proc. SPIE-Int. Soc. Opt. Eng., 1986. **631**(Adv. Resist Technol. Process. 3): p. 124-34.
6. Yeh, T.F., H.Y. Shih, and A. Reiser, "*Percolation view of novolak dissolution and dissolution inhibition,*" Macromolecules, 1992. **25**(20): p. 5345-52.
7. Tsiartas, P.C., et al., "*Mechanism of Phenolic Polymer Dissolution,*" Macromolecules, 1997. **30**(16): p. 4656-4664.
8. Flanagin, L.W., et al., "*Probabilistic model for the mechanism of phenolic polymer dissolution,*" Proc. SPIE-Int. Soc. Opt. Eng., 1998. **3333**(Pt. 1, Advances in Resist Technology and Processing XV): p. 268-277.
9. Schmid, G.M., *Understanding molecular scale effects during photoresist processing*. PhD thesis, The University of Texas at Austin, 2003.
10. Israelachvili, J.N., *Intermolecular and surface forces : with applications to colloidal and biological systems*. 1985, London ; Orlando, [Fla]. Academic Press. xv, 296 p.
11. Burns, S.D., et al., "*Advancements to the critical ionization dissolution model,*" J. Vac. Sci. Technol., B, 2002. **20**(2): p. 537-543.
12. Schmid, G.M., et al., "*Electrostatic effects during dissolution of positive tone photoresists,*" J. Vac. Sci. Technol., B, 2002. **20**(6): p. 2913-2919.
13. Flanagin, L.W., et al., "*Mechanism of Phenolic Polymer Dissolution: Importance of Acid-Base Equilibria,*" Macromolecules, 1999. **32**(16): p. 5337-5343.
14. Verdier, P.H. and W.H. Stockmayer, "*Monte Carlo calculations on the dynamics of polymers in dilute solutions,*" J. Chem. Phys., 1962. **36**: p. 227-35.
15. Colburn, M.E., *Step and flash imprint lithography: a low-pressure, room-temperature nanoimprint lithography*. PhD thesis, The University of Texas at Austin, 2001.
16. Van Oss, C.J., R.J. Good, and M.K. Chaudhury, "*Additive and nonadditive surface tension components and the interpretation of contact angles,*" Langmuir, 1988. **4**(4): p. 884-91.
17. Mugele, F. and J.-C. Baret, "*Electrowetting: From basics to applications,*" J. Phys.: Condens. Matter, 2005. **17**(28): p. R705-R774.