Impact of photoresist composition and polymer chain length on line edge roughness probed with a stochastic simulator

Alexander Philippou
Thomas Mülders
Qimonda Dresden Gmbh and Company OHG
Königsbrücker Strasse 180
01099 Dresden, Germany
E-mail: Alexander.Philippou@qimonda.com

Eckehard Schöll
Technische Universität Berlin
Institut für Theoretische Physik
Hardenbergstrasse 36
10623 Berlin, Germany

Abstract. The impact of various parameters such as photoacid generator (PAG) concentration, acid diffusion length, and polymer size on the finally obtained line edge roughness (LER) in chemically amplified photoresists are investigated with a stochastic simulator. A new aspect of the simulations is to start with a polymer matrix modeled by molecular dynamics simulation and subsequently simplify the description of the resist composition for mesoscopically simulating the post-exposure bake (PEB) and development steps. The results show that decreasing the molecular weight (MW) of chain-like polymers does not necessarily lead to lower roughness values. Acid-breakable polymers are simulated as well showing that they can lead to improved LER characteristics.

Subject terms: photoresists; line edge roughness; polymers; mesoscopic simulator; lithography.

Paper 07026R received Apr. 3, 2007; revised manuscript received Jul. 12, 2007; accepted for publication Jul. 23, 2007; published online Dec. 3, 2007.

1 Introduction

This work investigates the various roughness effects arising in photoresist with a mesoscopic simulator, which has been developed under the aspect of the increasing importance of line edge roughness (LER) as a limiting factor in future lithography, especially for the extreme ultra-violet (EUV) regime. Its need arises from the problem that current continuous resist models simulate on a macroscopic scale and thus fail to estimate or predict roughness effects. While microscopic models, e.g., molecular dynamics simulation, can be employed to accurately describe polymer properties, they are limited to simulation regions of only a few nanometers with long computation times. Therefore, a mesoscopic simulator was developed, closing the gap between the microscopic and macroscopic regime. Although some models already exist for determining LER, a new aspect of the current work is the preparation of a different resist matrix, which serves as an input to post-exposure bake (PEB) and development simulations. Although the methodology for PEB and development simulations (to be discussed later on in detail) is based on a mesoscopic description that neglects structural details on an atomic length scale, the local density variations and the spatial arrangement of deprotection and ionization sites inside the resist volume can be expected to strongly influence the simulation results. Therefore, we decided to model the resist volume in a first step as detailed as possible by employing molecular dynamics simulation (MD) and to subsequently simplify the description of the resist composition for simulating PEB and development steps. We compare these results to the standard approach of polymer generation by a self-avoiding random walk, and show that similar trends can be obtained. The computation of the deprotection and ionization reactions during PEB and development is done by simulating a master equation, where an additional critical ionization (CI) level is introduced to model the polymer dissolution. In the resulting resist profile, frequency and height correlation analysis can be used to characterize not only the roughness but also critical exponents and correlation lengths.

The work is organized as follows. Section 2 starts by explaining some details of the MD simulations leading to the formation of the resist matrix. A short description of the PEB module is given in Sec. 3, while more detailed explanations on the development module are treated in Sec. 4. The following part of the work then deals with variations of the simulated resist matrix and the analysis of the respective simulation results. In Sec. 5 the polymer size and the concentrations of photoacid generator (PAG) are varied to predict LER trends and discuss the effects observed in simulation. Section 5 also treats some details of the analysis method applied. We further investigate the impact of main-chain scission on LER in Sec. 6 and additionally vary the diffusion coefficient.

2 Molecular Dynamics Simulation

For the MD simulation, the molecular modeling tool kit (MMTK) together with Visual Molecular Dynamics (VMD) was used. The model polymer poly(4'-tertbutoxycarbonyloxy styrene) (PBOCST) was added to the database and the simulation volume was prepared as shown in the Appendix in Sec. 8. PBOCST was chosen because it served as a standard polymer used in previously developed simulators (see Ref. 8). In this polymer, only protected or unprotected side chains occur where the unprotected side chains can be ionized during the development reaction. Here only a fully protected polymer was used for the MD simulation. Additional photoresist species such as PAGs,
base, and solvent were neglected. The PAG was assigned later for the post-exposure bake as additional cell contents. The position of the oxygen atom at the bottom of the benzole ring was taken as the reference coordinate, which localizes the protection group. For the later development step, the same coordinate was used for the position of the ionization reaction. A sketch of the molecular repeat unit is shown in Fig. 1. The resulting molecular volume is displayed in Fig. 1. More details on the MD simulation can be found in the Appendix in Sec. 8.

For the PEB and development simulation, a superlattice with cubic grid cells of length 0.8 nm was superposed to the periodically expanded MD box, and protection groups corresponding to a polymer were assigned to the positions of the previously mentioned oxygen atom. Along the resist plane, periodic boundary conditions were applied, whereas at the resist bottom and top, reflecting boundary conditions were used. For polymers created with the MD simulation, only those polymers extending the simulation volume at the top and bottom boundary were removed.

### 3 Stochastic Post-Exposure Bake

The PEB simulation has been described in detail in Ref. 11. In addition to the description in Ref. 11 the positions of the deprotection groups resulting from the MD simulation are assigned to the cells of the simulation superlattice. In this way, different cells with a typical side length of 0.8 nm contain a varying number of deprotection groups. Whenever an acid-catalyzed reaction occurred, it was assigned to the repeat unit of the polymer in the corresponding cell, which then was deprotected.

### 4 Stochastic Development Simulation

The stochastic development model applied is based on the “critical ionization model” plus the randomized polymer structure, which is the outcome of the MD and PEB steps. During the previous post-exposure bake step some of the polymer sites remain protected with intact blocking groups. The other sites can be easily ionized in an aqueous base developer solution while the protected sites cannot. Thus, regarding the development process, the resist can be treated as a two level system, with the polymer sites being in either of two states, ionized or neutral, while the protected sites do not participate directly in the reaction process. According to the “critical ionization model” (CI), a polymer is dissolved if a certain fraction of ionized sites is exceeded. Thus, although the protected sites are not involved directly in the reaction process, they do have influence, as a strongly protected polymer is unlikely to meet the critical ionization criterion.

#### 4.1 Stochastically Simulating the Chemical Reactions of the Critical Ionization Model

The ionization reaction for a polymer of length $M$ with $k$ protected sites and $l$ ionized sites reads

$$T_k H_{M-l} l + OH^- \rightleftharpoons T_k H_{M-l+1} l_{l+1} + H_2O, \quad (1)$$

where $T$ symbolizes the protected sites, $H$ the nonprotected sites, $l$ the ionized sites, $OH^-$ the reacting hydroxide group of the aqueous base, and $H_2O$ the resulting water molecule after the ionization. If more than a certain fraction (the critical ionization level) of polymer sites are ionized, the polymer is dissolved. During the creation of the superlattice (see Sec. 2), a list is established that links the individual polymer sites to corresponding cells and vice versa. A second list contains labels that identify the polymer to which a single site belongs. As is discussed later in more detail, the probability of a reaction of type 1 to occur in a lattice cell depends strongly on the cell contents. Thus, each cell is also assigned a “reactivity,” which is a measure of this reaction probability. Then each cell is assigned to a “logarithmic class.” Each such class collects cells with similar reactivities, which is useful for speeding up the simulation. The links between lists and lattice are shown in Fig. 3.

Each cell contains information on the total number of ionized, neutral, and blocked sites of the polymers that run through it. A system state $n$ can be defined, which is characterized by the number of ionized and neutral sites in all of the cells that are in contact with the developer solution. However, not all of the cells are accessible to the developer solution. To account for this fact, a “reaction front” collecting all accessible cells has to be incorporated into the simu-

---

**Fig. 1** The repeat unit of the modeled PBOCST where, the oxygen atom is shown to which the deprotection reaction during PEB and the ionization reaction during development has been assigned.

**Fig. 2** The resulting compressed volume with a boxlength of 43 Å where six polymers with 40 repeat units each are displayed. The polymer backbone atoms are displayed as spheres. The figure was created with VMD.¹⁰
luation. Then the system state is solely characterized by the number of ionized and neutral sites in the cells belonging to the reaction front.

It is assumed that the diffusion of the developer into the resist takes place on time scales much shorter than the reaction time scales (which will be the case if always enough \( \text{OH}^- \) ions are existent at the resist boundary). In the beginning of the dissolution process, the reaction front contains lattice cells at the top of the resist down to a certain penetration depth. As the simulation time evolves, the reactions in Eq. (1) take place, and more and more polymers meet the critical ionization criterion and are removed. When a cell contains no more polymers, it is developed and all nearest-neighbor cells become part of the reaction front. If one of the added cells is already empty, additional nearest-neighbors of the empty cell are added as well. Thus, by development of a cell content, other (neighboring) cells that could not be reached before by the developer solution then become accessible. Finally, at the end of the development, the cluster of nondeveloped lattice points still connected with the substrate is identified and displayed as the final resist profile. Note that for a sufficient percolation of the developer front, an appropriate number of void cells must exist in the simulation region. While in other simulators this number can be adjusted, here it is given by the combination of the resolution of the superlattice (here 0.8 nm) and the position of the oxygen atom resulting from the MD simulation.

4.2 System Properties and Cell Reactivities

At each instant of time, the system to be simulated is made up of all the reaction front cells that are in contact with the developer. If a lattice cell becomes empty because all of its cell content has been dissolved, a new system is defined by the resulting new reaction front. The total size of the system to be simulated is defined by all cells contained within the reaction front. The only chance of this system to leave its state \( n \) and enter a new state \( n' \) is through an ionization or neutralization of a polymer site in a certain cell. To model this type of system, the transition rates of the system are to be computed for each state \( n \). It is assumed that the rate \( W_n \) with which the state \( n \) can be left is proportional to the number of accessible ionized and neutral sites, respectively,

\[
W_n \sim k_1 [\text{OH}]^{-}[\text{H}] + k_2 [\text{H}_2\text{O}][\text{I}],
\]

where \([\text{H}]\) and \([\text{I}]\) denote the total numbers of accessible neutral and ionized sites, and \( k_1 \) and \( k_2 \) are the rates for the forward and backward reactions. Since the number of accessible ionized and neutral sites can be split into a sum over cells belonging to the reaction front,

\[
[H] = \sum_i [H], \quad [I] = \sum_i [I],
\]

the overall rate \( W_n \) can be partitioned into a sum over cell reactivities

\[
W_n = \sum_i (k_1 [\text{OH}]^{-}[\text{H}] + k_2 [\text{H}_2\text{O}][\text{I}]) = \sum_i w_i,
\]

where \( w_i = k_1 [\text{OH}]^{-}[\text{H}] + k_2 [\text{H}_2\text{O}][\text{I}] \) denotes the cell reactivity in lattice cell \( i \). In this way, each cell contributes to the total rate \( W_n = \sum_i W_{n,i} = \sum_i w_i = W_{f,n} + W_{n,n} \), which itself consists of the total ionization rate \( W_{f,n} \) and the total neutralization rate \( W_{n,n} \). The various types of reactivities are listed in Table 1.

The system can be modeled within the framework of Monte Carlo simulations. Introducing the notation \( p(n,t|n') \), which describes the conditional probability for the system to be found in state \( n \) at time \( t \) provided it had been in state \( n' \) at time \( t = 0 \), the time evolution, is governed by a master equation

\[
\frac{\partial}{\partial t} p(n,t|n') = \sum_{n''} [W_{n'' \rightarrow n} p(n'',t|n') - W_{n \rightarrow n''} p(n,t|n'')],
\]

where \( W_{n \rightarrow n'} \) denotes the transition rate from state \( n \) into the new state \( n' \). In Eq. (5), not only all possible transitions to leave the state \( n \) but also all transitions to enter the state \( n \) are taken into account. Thus the master equation is a balance equation describing the time evolution of the conditional probability by adding up all possible ways of entering or leaving the actual state \( n \).
4.3 **Simulating the Master Equation**

The master equation can be simulated with the Gillespie algorithm. Assuming the system to be in state \( n \) within a time interval \([t_0, t_1]\), the probability to be in any other state \( n' \) vanishes. For that time interval, the master equation reduces to

\[
\frac{\partial}{\partial t} p(n,t|n,t_0) = -W_n p(n,t|n,t_0), \tag{6}
\]

As the system at time \( t_0 \) was in state \( n \), Eq. (6) has to be solved with the initial condition \( p(n,t_0|n,t_0)=1 \). This yields

\[
p(n,t|n,t_0) = \exp[-W_n(t-t_0)]. \tag{7}
\]

As this is the probability to find the system after the elapsed time \( t-t_0 \) in the state \( n \), 1 \(-p(n,t_1|n,t_0)\) is the probability to leave the state. Considering the case of an infinitesimal time interval \( t_1 \leq t \leq t_1+dt \), in which a possible transition could occur, leads to a probability density

\[
\rho(t_1)dt_1 = \left[1-p(n,t_1|n,t_0)\right]dt_1 \tag{8}
\]

\[
= -W_n \frac{d}{dt_1} \exp[-W_n(t_1-t_0)]. \tag{9}
\]

The transition time interval \( \delta t=t_1-t_0 \), after which a change of system state takes place, is thus exponentially distributed and can be modeled with a set of random numbers drawn from \( W_n \exp(-W_n \delta t) \). This property is a key feature of the Gillespie algorithm.

Exponentially distributed random numbers can be generated from uniformly distributed random numbers in the interval \([0,1]\). Thus, the time interval after which a transition takes place can be simulated by

\[
\delta t = -\frac{1}{W_n} \ln(1-r), \tag{11}
\]

where \( r \) is drawn from uniformly distributed random numbers. Therefore, the algorithm in a simplified form consists of the following.

1. Initialize: create proper start distribution at \( t=0 \) in state \( n^0 \) and evaluate all reactivities of accessible cells, set up reaction front.
2. Advance time step after Eq. (11).
3. Select randomly the next reacting cell among the accessible ones according to its reactivity weight.
4. Choose a reacting polymer inside the cell according to its reactivity weight.
5. Choose reaction (either ionization or neutralization) according to its reactivity weight.
6. Actualize reaction front and reactivities.

The problem with this modeling approach is the computation time. As the complete list of accessible cells can be huge, it is very time consuming to search a reacting cell within this list. A faster alternative is described in the following.

4.4 **Von Neumann Rejection**

The von Neumann rejection scheme is particularly useful when dealing with a large number of cells out of which a possible reacting cell is to be drawn. The main mechanism is shown in Fig. 4(a).
Labeling of an accessible cell within the reaction front by \( x \), a relative reaction probability, can be assigned to each accessible cell

\[
p(x) = \frac{w(x)}{W_n}, \quad W_n = \sum_{x'} w(x').
\]  
(12)

Defining a “trial function” \( \alpha \),

\[
\alpha = \max \{ p(x) \} \forall x,
\]  
(13)

the following von Neumann rejection scheme can be applied to draw a cell from \( p(x) \) without searching the whole list.

1. Draw two random (uniformly distributed) numbers \( r_1, r_2 \) independent from each other and calculate,

\[
x := Nr_1,
\]  
(14)

\[
y := \alpha r_2,
\]  
(15)

where \( N \) is the length of the cell list.

1. Accept \( x \) as a possible reacting cell if

\[
y \leq p(x),
\]  
(16)

otherwise reject it and go to step 1.

Whether this cell selection algorithm works fast depends on the acceptance ratio \( \nu \), given by

\[
\nu = \frac{\int_0^1 dx p(x)}{\int_0^1 dx \alpha(x)}.
\]  
(17)

Therefore the cell reactivities within the list should not differ too much from each other, and the cell list should be within reasonable length. Otherwise, the acceptance ratio would be \(<50\%\). To overcome this problem, logarithmic classes are implemented.

### 4.5 Logarithmic Classes

A logarithmic class is built up of cell reactivities \( w_v \), where in each class the reactivity differs by a factor of less than 2, such that

\[
2^{k-1} < w_v \leq 2^k.
\]  
(18)

The class \( (k) \) contains all cells \( v \) with reactivity \( w_v \), which satisfy the previous equation. The overall reactivity in class \( k \) is then defined as

\[
w^{(k)} := \sum_{v \in (k)} w_v,
\]  
(19)

with the total rate being

\[
W_n = \sum_k w^{(k)}.
\]  
(20)

It can be seen that by this sorting trick, the acceptance ratio is significantly increased as shown in Fig. 4(b). When back-pointers are introduced, linking the cells and classes, the computation time is reduced from \( L^2 \) to \( L \log(L) \), where \( L \) describes the system size. As \( L \) is typically in the order of \( 10^5 \), the gain in computation efficiency is large.

### 4.6 Complete Algorithm

A simplified flow diagram of the algorithm can be seen in Fig. 5. The whole algorithm then consists of the following.

1. Calculate time step after Eq. (11).

2. Choose reacting class \( k \) with uniformly distributed random number \( r_1 \), such that,

\[
w_i = W_n r_1.
\]  
(21)

Subtract subsequently from \( w_i \) the class reactivities \( w^{(k)} \)

\[
w_i \leftarrow w_i - w^{(k)}
\]  
(22)

and accept class \( k \) if \( w_i \) becomes negative for the first time.
3. von Neumann rejection scheme: select reacting cell by choosing random numbers \( r_2 \) and \( r_3 \) independent from the first and compute

\[
v = \lfloor mr_2 \rfloor + 1, \quad y = 2^k r_3,
\]

where \( m \) denotes the number of cells in class \( v \), and \( \lfloor mr_2 \rfloor \) stands for the nearest integer smaller or equal to \( mr_2 \). Accept if \( y \leq w_v \). If cell \( v \) is accepted, continue; otherwise, repeat step 3 with new random numbers.

4. Select reacting polymer in cell \( v \) with random number \( r_4 \) by subsequently subtracting polymer ionization reactivities \( W_{p} \), such that

\[
c_i = w_{p}(k)r_4, \tag{24}
\]

\[
c_i \leftarrow c_i - W_{p} \quad \forall \ p \in [1, \ldots q], \tag{25}
\]

where \( q \) denotes the number of polymers in cell \( v \). Accept ionization in cell \( v \) when \( c_i < 0 \) for the first time. If \( c_i > 0 \) after subtraction of all ionized \( q \) polymers, continue with subtracting neutralization reactivities \( W_{N} \) until \( c_i < 0 \), meaning that an ionized site in polymer \( p \) in cell \( v \) is neutralized.

5. If a polymer is ionized and exceeds the critical ionization level, the polymer is removed from the lattice and its reacting sites removed from all lattice points it came across. If a lattice cell contains no more polymers, the lattice point is dissolved. Add surrounding cells to the reaction front, and sort surrounding cells into appropriate logarithmic classes.

6. Actualize cell reactivities; if necessary, move cell into appropriate new class that satisfies Eq. (19).

5 Application of the Combined Molecular Dynamics, Post-Exposure Bake, and Development Simulations

To investigate the impact of acid diffusion length and PAG concentration on the final profile, an aerial image with a rather high contrast of \( c \approx 0.8 \) was created, where around 9% flare was added. An ideal aerial image with infinite resolution was not chosen to yield more realistic conditions. Although the flare level of current EUV tools is at \( \sim 16\% \), around 8% are targeted for production, which is close to the value used here. The aerial image and continuous PAG concentration was calculated with the commercial Solid EUV software (Synopsys, Hillsboro, Oregon), where a 2-D Kirchhoff approximation for a binary mask was used. The numerical aperture (NA) was set to 0.25, \( \sigma=0.6 \), and \( D\text{illC}=0.30 \) cm\(^2\)/mJ with circular illumination and a mask pitch of 120 nm for 60-nm lines. For all simulations, the PEB time was set to 90 s and the development time to 30 s. A detailed list of the parameters varied during PEB and development is shown in Table 2. The resist dimensions are of 120 nm width, 80 nm length, and 88 nm height at a cell resolution of 0.8 nm, such that 1.65 million cells were used for the simulation. The obtained initial normalized PAG density averaged along the line compared to a continuous PAG density from Solid EUV is shown in Fig. 6, together with the normalized intensity. The initial PAG density is obtained by distributing the PAGs randomly over the whole simulation region, where only one PAG molecule is allowed per cell. The continuous PAG concentration is then interpreted in terms of a survival probability per PAG molecule, leading to a high survival probability in regions of low intensity and vice versa.

5.1 Performance

All calculations were carried out on a Linux 64-bit cluster on AMD Opteron 2.4 GHz processors. The computation

<table>
<thead>
<tr>
<th>Module</th>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>Resolution</td>
<td>0.8 nm</td>
</tr>
<tr>
<td></td>
<td>Simulation Vol.</td>
<td>( 120 \times 80 \times 88 ) nm(^3)</td>
</tr>
<tr>
<td>PEB</td>
<td>Deprotection ( k_1 ) [nm(^3)/s]</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Spontaneous acid loss ( k_2 ) [1/s]</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Acid-base neutr. ( k_3 ) [nm(^3)/s]</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Diffusion coefficient [nm(^2)/s]</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>PAG concentration [1/nm(^3)]</td>
<td>0.25–0.4</td>
</tr>
<tr>
<td></td>
<td>Dill C [cm(^2)/mJ]</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Polymer size [RU]</td>
<td>10–60</td>
</tr>
<tr>
<td>Development</td>
<td>Ionization rate [1/s]</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Neutralization rate [1/s]</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Critical ionization level</td>
<td>50%</td>
</tr>
</tbody>
</table>

Fig. 6 Initial PAG density taken as input for the PEB simulation compared to the underlying continuous PAG distribution and the aerial image averaged along the line.
The standard deviation between a resist height of 11 to 62 nm were considered. The roughness has been analyzed by fitting to a plane along the sidewall for MD based polymers of 40 r.u. size and $D=2.5 \text{nm}^2/\text{s}$. The colorbar shows the deviation from the plane in nanometers.

![Fig. 7 Resulting height profile when fitting to a plane along the sidewall for MD based polymers of 40 r.u. size and $D=2.5 \text{nm}^2/\text{s}$. The colorbar shows the deviation from the plane in nanometers.](image)

time for the PEB was at around 60 s. A comparable continuous simulation at the same resolution with Solid EUV at ten time steps yields $\sim 6$ s. While for cell numbers $\approx 100,000$, the stochastic simulation time is comparable to a continuous simulation. The computing time of the stochastic PEB increases for large cell numbers. This is mainly because of the many stochastic diffusion steps resulting due to the high spatial resolutions necessary for the development, which slow down the algorithm considerably. A speed-up can be obtained by running the PEB on a lower resolution and then switching to a high resolution for the development. For the development step, a simulation took around 12 s and is within a factor of 3 when compared to the $\sim 4$-s computation time of continuous development. Here the benefit of using logarithmic classes is visible. We conclude that the mesoscopic model is with a total computation time of $\sim 70$ s for 1.65 million cells, suitable for resist calculations.

### 5.2 Roughness Evaluation

The roughness has been analyzed by fitting to a plane along the resist sidewall, as shown in Fig. 7, where only points between a resist height of 11 to 62 nm were considered. The standard deviation $\sigma$ was determined by calculating the height-height correlation function in 2-D,

$$C(r) = \left\langle [z(x)-\bar{z}] [z(x+r)-\bar{z}] \right\rangle_x,$$  \hspace{1cm} (26)

following the approaches in Refs. 17–21. Here $x$ is the position vector in the plane of the sidewall and $z(x)$ is the distance normal to the sidewall. $\bar{z}$ is the mean value. The brackets stand for averaging over all position vectors $x$. The obtained 2-D correlation function was then averaged over all azimuthal positions to obtain $C(r)$, depending only on the radius value $r=|r|$. Note that per definition, $C(0)=\sigma^2$. Similar, the height-difference correlation function for determining correlation lengths and critical exponents is defined by

$$H(r) = \langle [z(x)-z(x+r)]^2 \rangle_x.$$  \hspace{1cm} (27)

Its average over all azimuthal positions was computed from $C(r)$ by $H(r)=2[C(0)-C(r)]$. Note that the saturation value of $H(r)$ corresponds to $2\sigma^2$ and scales as $H \sim r^{2\alpha}$ if $r \ll l_c$, where $\alpha$ is the critical exponent describing the scaling behavior of the sidewall roughness, and $l_c$ is the correlation length. This implies that an increase of the critical exponent $\alpha$ also results in larger local height differences.

### 5.3 Impact of Polymer Size at Constant Photoacid Generator and Constant Diffusion

We start by considering the case of a high PAG concentration of 13% and no base, thus the sidewall roughness is only limited by polymer size and diffusion length. Due to the high PAG concentration and the high CI level of 50%, the resist is in an acid-saturated regime where lowering the diffusion length results in more resist loss. First the dose was fixed at 16 mJ/cm², such that the amount of acid generated was kept constant. The CD of the resulting line varies for different polymer lengths as resist solubility is changed, which was already reported in Ref. 22. To obtain a similar range of CD values for different polymer generation methods, some parameters for polymers distributed by a self-avoiding random walk had to be changed. The $k_1$ value was set to 0.9 nm²/s and the CI value to 60%. Furthermore, $D$ was set to 2.5 nm²/s for MD-based polymers and to 3.0 nm²/s for polymers distributed by a self-avoiding random walk, thus an offset between the different diffusion coefficients of 0.5 nm²/s was applied. The reason for the major differences between the two polymer generation methods is the distribution of void cells. The void cells are distributed periodically for the case of the MD-generated polymers and at random for polymers generated by a self-avoiding random walk. As is seen later, this also affects the critical exponents and correlation lengths. The CD here increases for increased polymer r.u. as resist solubility is changed. As the developer percolates through the resist, larger polymers are not as easily enclosed, as smaller ones leading to an offset between 10 and 60 repeat-unit (RU) polymers of around 8 nm for self-avoiding random walk polymers, which yields 46 nm $< CD < 54$ nm for increasing RU, and similar 42 nm $< CD < 58$ nm for MD-based polymers. All 3σ values for the different repeat units for the polymers are shown in Fig. 8. Note that for each point, an average of more than 10 simulations was used. As can be seen, lower MW polymers with 20 to 30 repeat units show the best performance where the lowest 3σ value found in our simulation corresponds to 5.3 nm for the MD-generated polymers and 6.0 nm for polymers generated by the self-avoiding random walk.

For larger polymers, roughness increases, which was observed in Refs. 22 and 23. To explain the increase in roughness for very low MW polymers, the degree of ionization (DOI) per polymer, i.e., the ratio of ionized groups per polymer over the number of repeat units, must be taken into account. While the mean DOI per polymer is approximately independent of the polymer length, the local fluctuations of the DOI is not. The reason being that longer...
polymers average over more polymer sites and therefore smooth out the number fluctuations. This is depicted in Fig. 9 for the MD-generated polymers and in Fig. 10 for self-avoiding random walk polymers. Here, the DOI for the whole simulation region was calculated. As can be observed, the average DOI remains approximately constant, while its standard deviation $3\sigma$ DOI (i.e., the number of fluctuations of ionized sites) increases for smaller polymers. The increase for the different polymer generation methods varies. For the MD-based polymers, it is linear, while for the random walk polymers, a larger increase for shorter polymers occurs. However, both methods lead to a tradeoff for reducing LER between decreasing the polymer grain size at the resist edge by lowering MW and minimization of statistical fluctuations by increasing MW.

A similar increase in LER for polymers 50 RU for the case of chemically amplified resists was found in Ref. 22. While in general our simulation results agree with Ref. 22 when using the same polymer distribution by a self-avoiding random walk, differences in the magnitude of the LER and exact shape of the curves are most probably related to the different aerial image and polymer matrix used. In Ref. 22 an ideal aerial image with a contrast of 1 was used with partially protected polymers, where the fraction of void cells $f_V$ was explicitly set to $f_V=0.10$. In the present work, the fully protected polymer structure and $f_V$ are either fixed by MD and the 0.8-nm superlattice and vary slightly for the different repeat units, namely $0.14\leq f_V \leq 0.16$ for 10 $\leq$ RU $\leq$ 40, or are fixed for the self-avoiding random walk polymers to $f_V=0.15$.

### 5.4 Critical Exponents and Correlation Length

To further analyze the simulated roughness, correlation lengths $l_c$ and critical exponents $\alpha$ have been calculated for MD-based polymers and for the self-avoiding random walk polymers. The two height-difference correlation functions for 10 and 40 RU MD-based polymers are displayed in Fig. 11. As the local fluctuations of the inhibitor concentrations after PEB are approximately independent on the number of repeat units, the following effects are mainly related to the polymer matrix and the development step. For the self-avoiding random walk polymers, $\alpha$ remained close to $0.26\pm0.02$, while the correlation length was at around $8.5\pm1$ nm, where no clear change of $\alpha$ or $l_c$ for different repeat units could be observed. All extracted correlation lengths and critical exponents for the MD-based polymers are shown in Fig. 12. As can be seen, $l_c$ increases for larger polymers, which implies that long-range interactions of the system scale with polymer size. This results from the distribution of void cells, which changes slightly for larger polymers. This changes the percolation of the developer through the resist matrix, as longer polymers are not as easily enclosed by the developer as shorter ones. To understand the change of $\alpha$, the relation $H\sim \rho^{2\alpha}$ (see Sec. 5.3) leads to the conclusion that larger polymers result in increased local height differences. This is simply due to the dissolved particle size being larger. $\alpha$ then reduces with decreasing polymer size. However, for 10 RU polymers,
the number fluctuations prevail over the decreasing grain size at the resist edge, which then is also visible by the increase of $a$.

All observed critical exponents in simulation are smaller than those normally found in experiments where $a$ is in the range of 0.4 to 0.6, as found in Ref. 24. This might result from several effects. First of all, a static polymer matrix was used here, but for real polymers, a reordering also occurs during PEB, which might affect acid diffusion and development, as the distribution of void cells is changed. Also, at the developer-resist interface, various reorderings might occur that change the final profile and therefore $a$. Furthermore, the polymer matrix used here is only an approximation to a real resist, which consists of much more functional groups and additional contents such as solvent and base. Further effects might be related to the measurement method. Here, a 3-D profile is analyzed while most critical exponents are commonly measured with a top-down scanning electron microscope (SEM). In the SEM, secondary electrons are utilized for detecting the feature, yielding a final 2-D image where a large signal at edge features is detected (where more secondary electrons are created). Thus an averaging over the sidewall occurs. Also, subsequent averaging filters applied during SEM profile evaluation might change the roughness. Finally, even for measurements with an atomic force microscope, effects from tip convolution can affect critical exponents.

### 5.5 Impact of Photoacid Generator Concentration at Constant Diffusion

Not only do the polymer size and acid diffusion length influence the final roughness, the PAG concentration was varied from 9 to 13% for polymer lengths of 10 to 30 repeat units for the MD-based polymers, as shown in Fig. 13, now keeping the diffusion length constant at $D=2.25$ nm$^2$/s. The dose was properly adjusted to keep the amount of acid generated constant, where the resulting target line width was $46 \pm 2$ nm for 10 RU polymers, $53 \pm 2$ nm for 20 and $55 \pm 2$ nm for 30 RU polymers. According to Ref. 11, lowering the PAG content introduces larger fluctuations in acid concentration. Thus in general, an increase in PAG concentration results in lower roughness. This trend was confirmed by the simulation results.

### 6 Acid Breakable Polymers

The idea of acid breakable polymers was first introduced in 1987 by Frechet et al.,$^{25}$ and recent attention was drawn to these systems by Eschbaumer et al.$^{26}$ in 2003, where im-

---

**Fig. 11** Height-difference correlation functions for 10 and 40 r.u. MD based polymers are shown. The increase in correlation length from 7 to 12 nm for large polymers is visible.

**Fig. 12** Correlation length $l_c$ and critical exponent $\alpha$ for all repeat units of the MD based polymers for $D=2.5$ nm$^2$/s are shown. The correlation length decreases for smaller polymers. The critical exponent decreases as well for smaller polymers whereas for 10 r.u. an increase can be observed.

**Fig. 13** Sidewall roughness $3\sigma$ as a function of increasing polymer size and PAG concentration for $D=2.25$ nm$^2$/s.
Improvements in LER of up to 30% were found. Although high glass transition temperature and etch stability for these polymer platforms remain an issue, our model was used to determine a theoretical potential in terms of LER. To model such a polymer, the acid molecules were allowed to break a polymer in the simulation, where a minimum polymer size can be defined that does not undergo any further scission reactions. For our simulations, a lattice consisting of 60 RU polymers distributed by a self-avoiding random walk was chosen, together with a minimum size after scission of ten repeat units. The remaining parameters equal those from the previous section, with a PAG concentration of 0.4 \( \text{J/m}^3 \), where now additionally the diffusion coefficient was varied between \( D=2.0 \text{ nm}^2/\text{s} \) to \( D=3.0 \text{ nm}^2/\text{s} \). Each polymer was allowed to undergo a scission reaction with a probability of \( p=0.2 \) if a deprotection reaction occurred at the inhibitor site. The resulting linewidth for the main-chain scission polymers decreased by about 6 nm when compared to the 60 RU polymers due to the previously mentioned percolation effect of the developer. The \( y \)-averaged polymer size distribution, together with the histogram of the number of polymers over polymer size, is depicted in Figs. 14 and 15. The resulting 3\( \sigma \) values are shown in Fig. 16. As can be seen in Fig. 15, the polymer size is changing locally with a large area of long chain polymers present near the unexposed region. For larger diffusion lengths, roughness increases for the 60 RU polymers. As the resist is in an acid-saturated regime as previously mentioned, and the amount of acid generated was kept constant, linewidth increases for larger diffusion coefficients. This degrades chemical contrast and by this increases roughness. However, the acid-breakable polymers perform much better for increasing diffusion coefficients and show a lower roughness than the 60 repeat units. At low diffusion lengths, the acid concentration during PEB remains high close to the exposed-unexposed interface. This results in a large fraction of small (acid-broken) polymers at the interface, in turn leading to large fluctuations of the DOI, i.e., large fluctuations of the relative number of ionized sites per polymer (see Sec. 5). This causes increased LER.

7 Conclusion

We demonstrate a complete modeling system that takes into account various roughness effects during the post-exposure bake and development process. These effects are based on polymer size and distribution, and PAG loadings. We compare a different polymer generation method based on molecular dynamics simulation to the standard approach of distributing polymers by a self-avoiding random walk, and show that similar results and trends can be obtained. But differences in critical exponents and correlation length exist, which result from periodically expanding the small MD volume to fill the whole resist volume. We further determine a roughness limit of 5 to 6 nm in terms of 3\( \sigma \) in simulation for single chain length polymers of 20 to 30 RU size, depending on the polymer generation method used. This is the same order of magnitude as experimentally observed LER. We also discuss the effect of different chain lengths...
lengths on the resulting roughness. This leads to a tradeoff between two main effects. First, larger polymers lead to a higher roughness, as the possible grain size at the resist edge is increased. Second, long polymers tend to average the fluctuations in the number of ionized groups over larger regions, and in this way minimize roughness. This latter effect smooths the resist profile for larger polymers. We further investigate the impact of main chain scission on the final sidewall roughness and compare it to 60 RU single chain length polymers distributed by a self-avoiding random walk. It is shown that acid breakable polymers can lead to lower sidewall roughness for fairly large acid diffusion lengths. If the etch stability and glass transition temperature of these systems can be improved, photoresists consisting of acid breakable polymers may become advantageous.

Acknowledgments

We thank M. Sebald and K. Eilani for detailed information on photopolymer chemistry and composition, as well as M. Block for helpful discussions on kinetic Monte Carlo simulation, critical exponents, and roughness control. We further thank S. Trogisch and W. D. Domke for information on current EUV tool technology. This work was financially supported by the Ministry of Education and Research of the Federal Republic of Germany (project number 01M3162). The authors are responsible for the content of the work.

Appendix: Molecular Modeling Details

The fully protected polymer poly(4-tert-butoxycarbonyloxy styrene) (PBOCST) was created within a large volume with a cubic unit cell of around 500 Å box length and periodic boundary conditions. Depending on the length of a single polymer between 6 and 24, further polymers with their center of mass set at random positions were added, such that a total of 240 RU was contained within the box. These numbers result from the fact that the MD box was slowly compressed to a length of 43 Å, allowing the molecules to relax at least 1000 fs between successive compression steps. Then a density of approximately 3 RU per nm² was reached. Note that 60 Ru polymers were tried to be simulated as well, but as only four polymers were contained within the 43 Å box, effects from periodically extending the MD box for the later PEB step yielded results that differ strongly from the results when polymers were distributed by a self-avoiding random walk. Thus a sufficient number of polymers must be modeled within a single MD box. Further settings for the MD simulation regarding the bond energies and distances between the different molecules were taken from the literature, and those bond energies missing were approximated. These bond energies are present in the literature, and those bond energies missing were approximated. These bond energies are present in the literature, and those bond energies missing were approximated. These bond energies are present in the literature, and those bond energies missing were approximated.

References
