The Generalized Characteristic Model for Lithography: Application to negatively chemically amplified resists

David Ziger, Chris Mack, Romelia Distasio
SEMATECH, Austin, TX 78741

ABSTRACT

A generalized approach towards modeling resist performance is introduced and applied towards characterizing a negative chemically amplified resist system. The Generalized Characteristic Model for Lithography is used to extract parameters to easily evaluate development rates from characteristic curves. The model suggests that two lumped parameters, $\alpha_n$ and $E_0$, dominate lithographic response for negative chemically amplified resists. Both $\alpha_n$ and $E_0$ were regressed from characteristic curves over a postexposure bake temperature and time range from 110-150°C and 30-90s and develop times from 30-150s. $E_0$ showed the predicted postexposure bake temperature and time and develop time dependencies over the processing window while $\alpha_n$ did not. Possible explanations for this discrepancy are discussed.

These parameters were used to simulate linewidths that were compared with experimental results. Linewidth predictions using the Generalized Characteristic Model agreed to within 15% of experimental results over the entire processing window.

1. INTRODUCTION

Chemically amplified positive and negative resists have demonstrated sub 0.5μm resolution and high sensitivity required for DUV and e-beam lithographies. Current modeling of these systems postulate acid catalyzed crosslinking of polyvinylphenol (PVP) or deblocking of polyvinylphenol derivatives for the dissolution inhibition mechanism for negative and positive versions respectively. Consequently, proposed kinetic mechanisms are quite different though their performance in terms of sensitivity and resolution are similar.

Negative chemically amplified resist systems have been modeled most frequently. Thackery et al proposed a mechanism for Shipley SNR248 which is an acid catalyzed negative resist whose base resin, PVP, is base soluble. Irradiation decomposes a photoacid generator (PAG) which in turn catalyzes the reaction of a melamine crosslinking agent with the PVP resin thus making it insoluble. Seligson and coworkers developed the concept of "effective dose" to correlate the effect of crosslinking bake kinetics on actual exposure dose. Fukuda and Okazaki evaluated kinetic parameters for crosslinking and simulated linewidths. Ferguson et al and Chiu et al have developed a generalized program to extract kinetic parameters from dissolution rate monitoring (DRM) data given proposed reactions.

In this paper, we apply the Generalized Characteristic Model to negative chemically amplified resists. In this general approach, the dissolution mechanism is assumed to be primarily influenced by the solubility of a dominant soluble species. For SNR248 and similar negative resists, this dominant soluble species is the concentration of unreacted PVP sites. We derive an expression for the concentration of the unreacted soluble site concentration and the rate of dissolution as a function of dose deposited in the film. Under conditions of minimal bleaching, absorption and surface dissolution effects, we can extract kinetic parameters from conventional characteristic exposure curves which relate remaining resist thickness after develop as a function of exposure dose.

Characteristic curves were carefully measured over a wide range of experimental conditions. Relevant parameters were then extracted from experimental characteristic curves for SNR248 and compared to model predictions. Finally, simulations were done using the regressed parameters and compared to experimental results over a wide range of conditions for SNR248.
2. THEORY

A detailed explanation of the Generalized Characteristic Model (GCM) for Lithography is given elsewhere. The objective of this approach is to model, measure and extract relevant processing parameters (e.g., postexposure bake and develop) from easily measured lithographic characteristic curves. These parameters are then used in simulation programs. We shall outline the approach specifically applied towards modeling negative chemically amplified resists.

The characteristic curve, \( \tau_N \), quantifies resist remaining after development as a function of incident exposure energy. For current practices of microlithography, resist loss occurs due to the postexposure bake effects and dissolution during development:

\[
\tau_N = 1 - \Delta \tau_{PEB} - \Delta \tau_{DEV}
\]  

where \( \tau_N \) is the remaining resist after development normalized to the initial film thickness, \( D \), and the subscripts \( PEB \) and \( DEV \) denote the postexposure bake and development processes respectively.

The resist is modeled as a mixture of base soluble, \([S]\), and insoluble, \([M]\) species. Both \( \Delta \tau_{PEB} \) and \( \Delta \tau_{DEV} \) are dependent on their relative concentrations. For negative chemically amplified resists \([S]\) is the concentration of unreacted host polymer (e.g., PVP). Since the effect of the postexposure bake insolubilizes the exposed regions via reaction of the host polymer matrix, \( \Delta \tau_{PEB} \) is assumed to be linearly dependent on the extent of conversion of \([S]\) to \([M]\):

\[
\Delta \tau_{PEB} = \Delta \tau_{(E=0)} + (1 - \frac{[S]}{[S_0]}) G
\]  

where \( \Delta \tau_{(E=0)} \) is the thickness change in the unexposed resist, \( G \) is the percentage thickness change at complete conversion and \([S_0]\) is the initial concentration of soluble sites.

Thickness loss during development, \( \Delta \tau_{DEV} \), is obtained by integrating the development rate over the time of develop:

\[
\Delta \tau_{DEV} = \frac{\int_0^{t_{DEV}} r_{DEV} dt}{D}
\]  

where \( r_{DEV} \) is the instantaneous develop rate. If absorption, bleaching and surface dissolution effects are minimal, then \( r_{DEV} \) can be assumed constant yielding:

\[
\Delta \tau_{DEV} = \frac{r_{DEV} t_{DEV}}{D}
\]
We assume that the development rate is proportional to the concentration of soluble sites raised to a power, \( n \), where \( n \) is a coordination number for the number of soluble sites which act in concert to influence solubility:

\[
\Delta \tau_{\text{DEV}} = \frac{k_{\text{DEV}} t_{\text{DEV}} [S]^n}{D}
\]  

(5)

The concentration of soluble sites, \([S]\), for chemically amplified negative resists is obtained from the extent of reaction of the acid catalyzed postexposure bake chemistry:

\[
\frac{d[S]}{d t_{\text{PEB}}} = -k_{\text{PEB}} [S] [H^*]
\]  

(6)

Since acid catalysis is involved \([H^*]\) is assumed to remain constant. Integrating Eq 6 yields:

\[
[S] = [S_0] e^{-k_{\text{PEB}} [H^*] t_{\text{PEB}}}
\]  

(7)

where \( k_{\text{PEB}} \) and \( t_{\text{PEB}} \) are the postexposure bake time and pseudo-first order rate constant respectively. We obtain \([H^*]\) from the photodecomposition of the photoacid generator (PAG):

\[
\frac{d[PAG]}{dE} = -k_{\text{photo}} [PAG]
\]  

(8)

where \( k_{\text{photo}} \) is the first order photodecomposition rate constant. (Note that \( k_{\text{photo}} \) is identical to the Dill C parameter.) Acid catalysis is sensitive to residual amine contaminants. We model this effect by supposing that all protons generated with an energy less than \( E_{\text{Inhab}} \) are neutralized by residual contaminants. If \([PAG_0]\) is the initial PAG concentration in the resist, then the fraction of \([PAG]\) remaining to generate protons for acid catalysis is (from Eq 8) \( 1 - e^{-k_{\text{photo}} E_{\text{Inhab}} } \). Consequently, the proton concentration available for catalysis is:

\[
[H^*] = [PAG_0] (e^{-k_{\text{photo}} E_{\text{Inhab}}}) (1 - e^{-k_{\text{photo}} (E_{\text{Inhab}} - E)})
\]  

(9)

Combining Eq 9, Eq 2 and Eq 7 and the result into Eq 1 provides an expression for \( \tau_N \) :

\[
\tau_N = 1 - \Delta \tau_{\text{PEB}} = \frac{k_{\text{DEV}} t_{\text{DEV}} [S_0]^n}{D} (e^{\alpha_n (1 - e^{-k_{\text{photo}} (E_{\text{Inhab}} - E)})})
\]  

(10)

Where:

\[
\alpha_n = e^{\frac{\text{Inhab}}{k_{\text{photo}} [PAG_0] k_{\text{PEB}}}}
\]

\[
\Delta \tau_{\text{PEB}} = \Delta \tau_{(E_0)} G(1 - e^{\frac{\text{Inhab}}{k_{\text{photo}} [PAG_0] k_{\text{PEB}}}})
\]

---

\(^a\)See Section 4.2 for comparisons of this develop model to other approaches. Daniels and Trefonas and Mack have applied the same approach towards modeling DRM data for positive photoresists.
The objective of the experimental work was to extract relevant parameters, \( \alpha_n \) and \( E_0 \), from measured characteristic curves under various postexposure bake and develop conditions. These parameters were used to evaluate TD. PROLITH/2 was modified to utilize \( \alpha_n \) and \( E_0 \) and used to simulate linewidths which were compared to experimental results.

Silicon wafers coated with SNR248 (Shipley, Marlbourough MA) resist on DUV-3 antireflection coating (Brewer Science, Rolla, MO) were exposed on a 0.35NA Laserstep KrF stepper (GCA Corp, Andover, MA). The actinic wavelength was 248nm. An antireflection coating was used to eliminate experimental error caused by resist thickness nonuniformities. Postexposure bake was done on MTJ Flexifab tracks followed by batch develop in 0.135 normal TMAH. Fig. 1 shows the two pass exposure pattern that was used. The first pass was a serpentine of increasing open frame exposures while the second pass interwove a serpentine of resolution die of increasing doses. Resist thickness measurements were taken at the open frame exposure sites. A SM200/E (Prometrix, Santa Clara, CA) was used to measure resist thickness after softbake and postexposure bake while a FT500 (Prometrix, Santa Clara, CA) was used to measure final resist thickness after develop. Using this technique \( \Delta \tau_{DEV} \) and \( \Delta \tau_{PEB} \) could be measured.

In addition to the wafers exposed according to Fig. 1, one exposure/focus wafer was also prepared to investigate focus predictions and compare to experiment.

Wafers with the pattern in Fig. 1 were processed at five postexposure bake temperatures and times and develop times. These wafers were processed randomly in the same day. This was done to minimize systematic error when comparing model predictions with experimental measurements of \( \alpha_n \) and \( E_0 \). Furthermore, the centerpoint conditions, \( T_{PEB} = 130^\circ C \), \( t_{PEB} = 60s \) and \( t_{DEV} = 90s \) were repeated six times to estimate the reproducibility of the experiment.

Therefore, if \( \alpha_n \) and \( E_0 \) can be extracted from \( \tau_N \), \( \tau_{DEV} \) can be easily evaluated. This rate expression can then be used in conjunction with lithography simulation programs to predict linewidths.

### 3. EXPERIMENTAL

At \( E = E_0 \), \( \tau_N = 0 \). Consequently, we can solve \( \frac{k_{DEV} r_{DEV}[S_0]^n}{D} \) in terms of \( E_0 \) yielding:

\[
\tau_N = (1 - \Delta \tau_{PEB} - (1 - \Delta \tau_{PEB}, E_0)] e^{-\alpha_n \left( e^{-k_{photo}E_0} - e^{-k_{photo}E_0^2} \right)}
\]

where \( \Delta \tau_{PEB}, E_0 \) is the thickness loss due to PEB at \( E_0 \). Consequently, the developing rate, \( r_{DEV} \), is:

\[
r_{DEV} = \frac{D}{t_{DEV}} (1 - \Delta \tau_{PEB}, E_0) e^{-\alpha_n \left( e^{-k_{photo}E_0} - e^{-k_{photo}E_0^2} \right)}
\]
Table 1. Range of $T_{\text{PEB}}, t_{\text{PEB}}, t_{\text{DEV}}$ Investigated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Postbake Temp</td>
<td>110</td>
<td>150</td>
</tr>
<tr>
<td>Postbake Time</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>Develop Time (s)</td>
<td>30</td>
<td>120</td>
</tr>
</tbody>
</table>

PROLITH/2 was modified to use the rate expression shown in Eq 12 to simulate profiles. The method of profile simulation using the Generalized Characteristic Model is discussed elsewhere. SNR248 properties used in the simulations are summarized in Table 2 along with appropriate references.

Table 2. SNR248 Simulation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{photo}}$</td>
<td>0.004</td>
</tr>
<tr>
<td>A ($\mu$m$^{-1}$)</td>
<td>-0.71</td>
</tr>
<tr>
<td>B ($\mu$m$^{-1}$)</td>
<td>1.10</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.80</td>
</tr>
</tbody>
</table>

3. RESULTS

Fig. 2a-c show experimental measurements of $\tau_N$, $\Delta\tau_{\text{PEB}}$, and $\Delta\tau_{\text{DEV}}$ as a function of incident dose resulting from SNR248 processed at the centerpoint conditions ($T_{\text{PEB}}=130^\circ\text{C}$, $t_{\text{PEB}}=60\text{s}$, $t_{\text{DEV}}=90\text{s}$). Data in Fig 2c ($\Delta\tau_{\text{DEV}}$ versus dose) were regressed to extract $\alpha_n$ and $E_0$ according to Eq 11 to evaluate the develop rate expression (Eq 12). Due to slight film loss during PEB, $\Delta\tau_{\text{PEB}}$ could not be measured precisely (see Fig. 2b). Consequently, we were unable to reliably regress $\alpha_n$ from $\Delta\tau_{\text{PEB}}$ data. Fig. 2a-c show data from one run along with regressions for $\tau_N$ and $\Delta\tau_{\text{DEV}}$. Simulations with Prolith/2 were done using $\alpha_n$ and $E_0$ parameters regressed from $\Delta\tau_{\text{DEV}}$. This rate expression resulted in the simulated profiles shown in Fig. 3b which were compared with experimental results (Fig. 3a).

Table 3 summarizes regressed $\alpha_n$ and $E_0$ parameters extracted from contrast curves generated over the design of experiment conditions. We were unable to regress $\alpha_n$ from $\Delta\tau_{\text{PEB}}$ due to negligible film loss. Table 4 compares experimental and PROLITH/2 simulated linewidth measurements using $\alpha_n$ and $E_0$ parameters extracted with the Generalized Lithography Model.
Fig. 2. a) $\tau_N$, b) $\Delta\tau_{PEB}$, and c) $\Delta\tau_{DEV}$ as a function of incident dose. Regression is shown for $\tau_N$ and $\Delta\tau_{DEV}$. 
Table 4. Measured and Simulated Linewidths

<table>
<thead>
<tr>
<th>Run</th>
<th>Dose (Mj/cm²)</th>
<th>Linewidth (µm)</th>
<th>% Dif</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured</td>
<td>Simulated</td>
</tr>
<tr>
<td>1</td>
<td>67.8</td>
<td>0.459</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>33.0</td>
<td>0.43</td>
<td>0.405</td>
</tr>
<tr>
<td>3</td>
<td>30.9</td>
<td>0.512</td>
<td>0.493</td>
</tr>
<tr>
<td>4</td>
<td>30.9</td>
<td>0.623</td>
<td>Scum</td>
</tr>
<tr>
<td>5</td>
<td>12.3</td>
<td>Scum</td>
<td>Scum</td>
</tr>
<tr>
<td>6</td>
<td>33.0</td>
<td>0.443</td>
<td>0.407</td>
</tr>
<tr>
<td>7</td>
<td>33.0</td>
<td>0.518</td>
<td>0.477</td>
</tr>
<tr>
<td>8</td>
<td>33.0</td>
<td>0.589</td>
<td>0.507</td>
</tr>
<tr>
<td>9</td>
<td>30.9</td>
<td>0.59</td>
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<td>10</td>
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<td>30.9</td>
<td>0.534</td>
<td>0.487</td>
</tr>
<tr>
<td>12</td>
<td>33.0</td>
<td>0.536</td>
<td>0.478</td>
</tr>
<tr>
<td>13</td>
<td>33.0</td>
<td>0.537</td>
<td>0.478</td>
</tr>
</tbody>
</table>

Linewidths were measured top down.

Linewidths greater than 0.6 were typically scummed when viewed from cross section.
Table 3. Characteristic Model Regression Results

<table>
<thead>
<tr>
<th>Run</th>
<th>$T_{PEB}$ (°C)</th>
<th>$t_{PEB}$ (s)</th>
<th>$t_{DEV}$ (s)</th>
<th>$\alpha_n\pm$Std Error</th>
<th>$E_0\pm$Std Error (mJ/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reproducibility Runs &amp; Constant $t_{PEB}\cdot t_{DEV}$ &amp; Constant $T_{PEB}\cdot t_{DEV}$ &amp; Constant $T_{PEB}\cdot t_{DEV}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>183.7±5.4</td>
<td>5.39±0.06</td>
</tr>
<tr>
<td>3b</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>198.1±6.6</td>
<td>5.64±0.04</td>
</tr>
<tr>
<td>3c</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>171.5±8.1</td>
<td>5.24±0.10</td>
</tr>
<tr>
<td>3d</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>186.7±6.6</td>
<td>5.48±0.07</td>
</tr>
<tr>
<td>3e</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>197.3±8.2</td>
<td>5.53±0.07</td>
</tr>
<tr>
<td>3f</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>172.8±5.4</td>
<td>5.28±0.06</td>
</tr>
<tr>
<td>1</td>
<td>110</td>
<td>60</td>
<td>90</td>
<td>65.0±2.8</td>
<td>12.0±0.18</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>60</td>
<td>90</td>
<td>110.3±3.4</td>
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<td>3b</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>185.0±6.7</td>
<td>5.43±0.07</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>60</td>
<td>90</td>
<td>197.0±9.4</td>
<td>4.08±0.09</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>60</td>
<td>90</td>
<td>216.2±6.2</td>
<td>2.56±0.04</td>
</tr>
<tr>
<td>7</td>
<td>130</td>
<td>15</td>
<td>90</td>
<td>107.7±2.4</td>
<td>7.71±0.06</td>
</tr>
<tr>
<td>8</td>
<td>130</td>
<td>38</td>
<td>90</td>
<td>134.8±5.2</td>
<td>5.69±0.09</td>
</tr>
<tr>
<td>3b</td>
<td>130</td>
<td>60</td>
<td>90</td>
<td>185.0±6.7</td>
<td>5.43±0.07</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>83</td>
<td>90</td>
<td>182.1±6.9</td>
<td>5.04±0.06</td>
</tr>
<tr>
<td>11</td>
<td>130</td>
<td>105</td>
<td>90</td>
<td>178.3±7.8</td>
<td>4.60±0.08</td>
</tr>
<tr>
<td>12</td>
<td>130</td>
<td>60</td>
<td>30</td>
<td>123.4±2.3</td>
<td>2.98±0.02</td>
</tr>
<tr>
<td>13</td>
<td>130</td>
<td>60</td>
<td>60</td>
<td>171.5±4.2</td>
<td>4.76±0.04</td>
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<td>3b</td>
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<td>60</td>
<td>90</td>
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<td>5.43±0.07</td>
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<tr>
<td>14</td>
<td>130</td>
<td>60</td>
<td>120</td>
<td>126.7±5.1</td>
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<tr>
<td>15</td>
<td>130</td>
<td>60</td>
<td>150</td>
<td>138.4±6.2</td>
<td>5.90±0.12</td>
</tr>
</tbody>
</table>

_bAverage of six runs_
4. DISCUSSION

4.1 Generalized Characteristic Model Form

The form of Eq 10-12 deserves further discussion. Let us consider the case in which $\Delta \tau_{\text{PEB}} = 0$. We first note that at extremes, both expressions obey realistic constraints. At $E = E_0$, $\tau_{\text{PEB}} = 0$ and $r_{\text{DEB}} = \frac{D}{t_{\text{DEB}}}$. The latter is the average rate through the bulk of the resist at $E_0$. At $E = -\infty$, $\tau_{\text{PEB}} = 1 - \Delta \tau_{\text{PEB},E_0}$ and $r_{\text{DEB}} = 0$ provided that $\alpha > 0$. By inspecting the definition of $\alpha_n$, this implies that the resist contains a photoacid generator and that both $k_{\text{PEB}}$ and $t_{\text{PEB}}$ are greater than 0. Consequently, conditions yielding larger $\alpha$ values increase the photoresist sensitivity. Assuming an Arrhenius temperature dependence for $k_{\text{PEB}}$ we see that this is tantamount to increasing the bake temperature or time or reducing residual contaminants in the resist:

$$\alpha = A \exp \left( \frac{E_a}{RT} \right) \left[ \text{PAG} \right] t_{\text{PEB}} \exp^{-k_{\text{photo}} E_{\text{fab}}}$$

where $A$ and $E_a$ are the Arrhenius pre-exponential factor and activation energy respectively.

4.2 Comparison with Other Models

There are several noteworthy comparisons between the Generalized Characteristic Model and other lithography models. First, $k_{\text{photo}}$ is identical to the $C$ parameter in the model for conventional resists proposed by Dill et al. The rate model ($r_{\text{DEB}} = [S]^n$) used to derive the Generalized Characteristic Model has been previously applied to conventional positive photoresists. Mack derived a general rate expression:

$$r_{\text{DEV}} = r_{\text{max}} \left( \frac{a+1}{a+(1-m)^n} \right) + r_{\text{min}}$$

For many photoresist systems, $a \gg 1$, which simplifies Eq 14 to:

$$r_{\text{DEV}} = r_{\text{max}} (1-m)^n + r_{\text{min}}$$

Since $[1-m]$ is the concentration of the base soluble carboxylic acid, we recognize that the develop model proposed here is consistent with Mack's provided $r_{\text{min}}$ is negligible. Development rate expressions equivalent to Eq 15 were also proposed by Daniels and Trefonas and Hirai, et al.

Ferguson et al. used a similar functional form for $r_{\text{DEV}}$ to model negative DUV resists:

$$r_{\text{DEV}} = R_0 (1 - CE_{(CS)})^a$$

where $R_0$, $C_0$ and $a$ are regressed from develop rate data and $CE_{(CS)}$ is obtained from acid catalyzed crosslinking kinetics. If $(1 - CE_{(CS)}/C_0)$ is an effective soluble species concentration, then this model is equivalent the one used in this paper.
4.3 Experimental and Predicted $\alpha_n$ and $E_0$ Dependencies

It is interesting to compare predicted and measured effects on both $E_0$ and $\alpha_n$. To investigate $E_0$, we solve Eq 10 for $E_0$:

$$E_0 = -\ln(1 + \frac{\ln(D/k_{DEV}t_{DEV}[S_0])^n}{\alpha_n n}) + E_{inhab}$$  \hspace{1cm} (17)$$

We can expand Eq 17 in a Taylor series:

$$E_0 = E_{inhab} + \frac{1}{k_{photo}} \left( \frac{\ln(k_{DEV}t_{DEV}[S_0]^n/D)}{\alpha_n n} - \frac{1}{2} \frac{\ln(k_{DEV}t_{DEV}[S_0]^n/D)}{\alpha_n n} \right) + \cdots$$  \hspace{1cm} (18)$$

Therefore, as a first approximation:

1. $E_0$ is linearly dependent on logarithm of develop time and initial resist thickness
2. $E_0$ is linear with the inverse of $\alpha_n$. Since $\alpha_n$ contains a rate constant, we expect $E_0$ to have an Arrhenius temperature dependence, that is the logarithm of $E_0$ should be linearly dependent on $1/T_{PEB}$. Also since $\alpha_n$ is linear in postexposure bake time, $E_0$ should be inversely proportional to $1/T_{PEB}$.

(Note that these are the same conclusions that can be obtained by approximating $1-e^{-k_{PE}(E-E_{photo})} = k_{photo}(E-E_{photo})$ in Eq 10 and then solving for $E_0$). Fig. 4a-c compare predicted dependencies of $E_0$ against experimental data.

From the definition of $\alpha_n$, we expect $\alpha_n$ to be linearly dependent on $t_{PEB}$, independent of $t_{DEV}$ and exponentially dependent on $1/T_{PEB}$. Fig. 5a-c show experimental results over the conditions employed. Note that $\alpha_n$ saturates as a function of higher postexposure bake temperatures (low $1/T_{PEB}$) and longer times. Furthermore, $\alpha_n$ varied somewhat randomly with $t_{DEV}$.

Comparing Fig. 4-5, it is apparent that the predicted trends for $E_0$ agreed better with experiment than those for $\alpha_n$. One explanation is that $n$ is processing dependent whereas the analysis above assumes a constant value. However we note that $E_0$ should be similarly affected. Another possible explanation is that there is an effective acid quenching mechanism at larger proton concentrations. The existence of a "acid loss" reaction has indeed been proposed by Ferguson et al.\textsuperscript{7} Consequently, $E_0$ follows the predicted $T_{PEB}$, $t_{PEB}$ and $t_{DEV}$ trends at low $[H^+]$, but quenching limits the insusubilizing reaction thus limiting $\alpha_n$ under conditions which should yield higher proton concentrations. In fact, close inspection of the Arrhenius plot (Fig. 4a) shows evidence for two activation energies above (2.6 kcal/mole) and below 130C (16 kcal/mole) while $\alpha_n$ is linear with $t_{PEB}$ at low times and levels off at longer times. The average activation energy calculated from $\alpha_n$ data below 130C (16kcal/mole) compares to 12kcal/mole regressed from $E_0$ data from 110-150C. It is interesting that the activation energy for $\alpha_n$ at lower extent of reactions (16 kcal/mole) and $E_0$ computed throughout the entire temperature range compare favorably with the measured sensitivity dose activation energy of 13.4 kcal/mole reported by Seligson and coworkers for a similar negative chemically amplified resist.\textsuperscript{3}
Fig. 4. Experimental $E_0$ dependence on a) $T_{PEB}$, b) $t_{PEB}$, and c) $t_{DEV}$ (error bars show ± one standard error).

Fig. 5. Experimental $\alpha_{fn}$ dependence on a) $T_{PEB}$, b) $t_{PEB}$, and c) $t_{DEV}$ (error bars show ± one standard error).
5. CONCLUSIONS

The application of the Generalized Characteristic Model for Lithography towards modeling negative chemically amplified resists is demonstrated. In this technique, relevant lumped parameters are extracted from experimental characteristic curves. These parameters are then used to evaluate effective develop rates in lithographic simulation. Simulated linewidths agreed within 15% of measured values over the entire processing window without using adjustable parameters. The dependence of the lumped parameters on process conditions was explored. \( E_0 \) followed the predicted trends of \( T_{PER} \), \( t_{PER} \) and \( t_{DEV} \) but \( \alpha_n \) did not. A possible explanation is that quenching of the \([H^+]\) catalyst at higher conversions causes this discrepancy.

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REFERENCES


