ABSTRACT

A mechanism for the development of positive optical photoresists is proposed, leading to the derivation of a development rate equation. This rate equation compares favorably with experimentally determined development rates. Typical values of the rate constants involved are given. Empirical models are given for the surface induction and substrate adhesion effects.

An overall positive resist processing model requires a mathematical representation of the development process. Previous attempts have taken the form of empirical fits to development rate data as a function of exposure (1, 2). The model formulated below begins on a more fundamental level, with a postulated reaction mechanism which then leads to a development rate equation. The rate constants involved can be determined by comparison with experimental data. Deviations from the expected development rates have been reported under certain conditions at the surface of the resist and near the resist-substrate interface. These effects, called the surface induction and substrate adhesion effects, respectively, can be related empirically to the expected development rate, i.e., to the bulk development rate as predicted by a kinetic model.

Bulk Development Model

In order to derive an analytical development rate expression, a kinetic model of the development process will be used. This approach involves proposing a reasonable mechanism for the development reaction and then applying standard kinetics to this mechanism in order to derive a rate equation. We shall assume that the development of a diazo-type positive photoresist involves three processes: diffusion of developer from the bulk solution to the surface of the resist, reaction of the developer with the resist, and diffusion of the product back into the solution. For this analysis, we shall assume that the last step, diffusion of the dissolved resist into solution, occurs very quickly so that this step may be ignored. Let us now look at the first two steps in the proposed mechanism. The diffusion of developer to the resist surface can be described with the simple diffusion rate equation

$$ r_D = k_D(D - D_s) $$

where $r_D$ = rate of diffusion of the developer to the resist surface, $D$ = bulk developer concentration, $D_s$ = developer concentration at the resist surface, and $k_D$ = rate constant.

We shall now propose a mechanism for the reaction of developer with the resist. The resist is composed of large macromolecules of resin $R$ along with a photoactive compound $M$, which converts to product $P$ upon exposure to UV light. The resist is quite soluble in the developer solution, but the presence of the PAC (photoactive compound) acts as an inhibitor to dissolution, making the development rate very slow. The product $P$, however, is very soluble in developer, enhancing the dissolution rate of unexposed resist.

The two steps outlined above are in series, i.e., one reaction follows the other. Thus, the two steps will come to a steady state such that

$$ r = r_D = r $$

Equating the rate equations, one can solve for $D_s$ and eliminate it from the overall rate equation, giving

$$ r = k_D k_D D^* $$

Using Eq. [3] and letting $m = M/M_s$, the relative PAC concentration, Eq. [5] becomes

$$ r = k_D D(1 - m)^n $$

When $m = 1$ (resist unexposed), the rate is zero. When $m = 0$ (resist completely exposed), the rate is equal to $r_{max}$ where

$$ r_{max} = \frac{k_D D}{k_M M_s + 1} $$

If we define a constant $a$ such that

$$ a = \frac{k_D D}{k_M M_s} $$

the rate equation becomes

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

There are three constants that must be determined experimentally, $a$, $n$, and $r_{max}$. The constant $a$ can be put in a more physically meaningful form as follows. A characteristic of experimental rate data is an inflection point in the rate curve at about $m = 0.3-0.7$ (see Fig. 1). The point of inflection can be calculated by letting

$$ \frac{d^2r}{dm^2} = 0 $$

giving

$$ a = \frac{(n + 1)(1 - m_{th})^n}{(n - 1)} $$

where $m_{th}$ is the value of $m$ at the inflection point, called the threshold PAC concentration.

This model does not take into account the finite dissolution rate of unexposed resist ($r_{min}$). One approach is simply to add this term to Eq. [9], giving

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

This approach assumes that the mechanism of development of the unexposed resist is independent of the above-proposed development mechanism. In other words, there is a finite dissolution of resist that occurs by a mechanism that is independent of the presence of PAC such a model, however, does not account for the increase in the development rate of unexposed resist as resist prebake temperature is increased.
shown that one effect of prebaking photosresists is the decomposition of the photoactive compound to a variety of products, one of which is thought to be identical to the exposure product $P_e$ (3). Thus, a second explanation of the unexposed development rate is due to an effective "exposure" of the resist during prebaking. For example, a 95°C, 1h convection oven prebake of Kodak 820 resist was found to decompose 15% of the photoactive compound in the resist (3). Also, the solvent content of the photosresist may affect development rate. Development rate data must be taken in order to further examine the mechanism of unexposed development.

**Experimental Data**

The rate constants $r_{\text{max}}$, $r_{\text{min}}$, $n$, and $m_{\text{TH}}$ must be determined in order to define the rate of dissolution of resist in the developer. From a resist processing point of view, $n$ can be thought of as a selectivity of the developer towards the exposed resist (Fig. 2). Higher values of $n$ result in higher selectivity. Of course, $m_{\text{TH}}$ describes the threshold effect of development. Values of $m < m_{\text{TH}}$ result in very high development rates, whereas values of $m > m_{\text{TH}}$ give very low development rates. Also, one should note that $r_{\text{max}}$ is dependent on the developer concentration $D$, but $m_{\text{TH}}$ and $n$ are independent of $D$. All parameters, however, are dependent on the resist and developer used. Experimental data collected by Dill et al. (1) for AZ1350J resist with 1:1 AZ developer (Fig. 1) are described very well by Eq. (11) using the values given in Table I. Although theoretical curves are not shown for comparison in Fig. 1, the fit to experimental data is within the uncertainty of the data.

The effect of prebake can be qualitatively explained with this model. The purpose of prebake is to dry the resist film by driving off solvents at elevated temperatures. An unfortunate consequence of these high temperatures, however, is the decomposition of the photoactive compound (3). Mathematically, this translates into a lower value of $M_e$ for higher prebake temperatures and times. The effect of this decomposition reaction on the development process will depend on the decomposition product formed (3). From the experimental data given by Dill (1), $r_{\text{max}}$ and $n$ decreased with increasing prebake temperature, $r_{\text{min}}$ increased, and $m_{\text{TH}}$ was unaffected.

**Induction and Adhesion Effects**

The kinetic model given above predicts the development rate of the resist as a function of the photoactive compound concentration remaining after the resist has been exposed to UV light. There are, however, several other parameters that are known to affect the development rate, but which were not included in this model. The two most notable deviations from the kinetic theory are the induction and adhesion effects. The induction, or surface inhibition, effect is a decrease in the expected development rate at the surface of the resist (4-6). The adhesion effect is a decrease in the development rate at the resist-substrate interface (5). Thus, these two effects are a function of the depth into the resist. The overall development rate can be divided into three regions as a function of depth into the resist (Fig. 3): the induction, bulk, and adhesion regions. The development rate in the bulk region can be predicted by the kinetic model above. The rates in the induction and adhesion regions, however, require a different description.

Several factors have been found to contribute to the surface induction effect, the most pronounced being deep-UV flood exposure. Doses in the range of several J/cm² at wavelengths of 200-300 nm have been found to cause cross-linking of the photosresist resin near the surface of the resist (5, 7). This technique is the basis for making resists thermally stable after patterning. Although flood-UV exposure is very effective in cross-linking the resin found in positive photosresists, it is not normally a part of resist processing before development. High temperature baking of the photosresist has been found to produce similar results and is also thought to cause cross-linking of the resin at the resist surface (4-6). In particular, prebaking the photosresist may cause cross-linking at some temperatures leading to the reduced development rate phenomenon (4, 6). Alternatively, the induction effect may be the result of reduced solvent

---

**Fig. 1. Experimentally determined development rates for AZ1350J in 1:1 AZ developer (1).**

**Fig. 2. Theoretical development rate curves as a function of the selectivity parameter $n$ (using $m_{\text{TH}} = 0.5$).**

**Fig. 3. General development rate curve showing surface induction and substrate adhesion effects.**

---

<table>
<thead>
<tr>
<th>Prebake at 70°C</th>
<th>Prebake at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{\text{max}} = 55 \text{ nm/s}$</td>
<td>$r_{\text{max}} = 21 \text{ nm/s}$</td>
</tr>
<tr>
<td>$n = 6$</td>
<td>$n = 5$</td>
</tr>
<tr>
<td>$m_{\text{TH}} = 0.61$</td>
<td>$m_{\text{TH}} = 0.61$</td>
</tr>
<tr>
<td>$r_{\text{min}} = 0.15 \text{ nm/s}$</td>
<td>$r_{\text{min}} = 2 \text{ nm/s}$</td>
</tr>
<tr>
<td>Predicted contrast $\gamma = 3.1$</td>
<td>Predicted contrast $\gamma = 2.3$</td>
</tr>
</tbody>
</table>
content near the resist surface. Of course, the degree to which this effect is observed depends upon the prebake time and temperature.

Figure 3 depicts a general development rate curve as a function of depth showing the induction effect. An empirical model can be used to describe both the positional dependence and the prebake dependence of the development rate. If we assume that development rate near the surface of the resist exponentially approaches the bulk development rate, the rate as a function of depth, \( r(z) \), is

\[
\tau(z) = r_\infty (1 - (1 - r_\infty e^{-\beta_2 z}))
\]

[12]

where \( r_\infty \) = bulk development rate, \( r_\infty \) = development rate at the surface of the resist relative to \( r_\infty \), and \( \beta_2 \) = an empirical constant. The induction effect has been found to take place over a depth of about 150 nm (4, 6), taken as the point at which the deviation from the bulk development rate has been reduced to 25% of its value at the surface of the resist (i.e., \( \exp(-\beta_2 z) = 0.25 \)). Thus, an appropriate value for \( \beta_2 \) is about 10 \( \mu \text{m}^{-1} \).

We shall assume that the value of the development rate at the surface of the resist, \( r_\infty \), is dependent on the prebake conditions. If we assume that the cross-linking reaction is first order, simple kinetics give us

\[
\tau(z) = \exp\left(-K(T)z\right)
\]

[13]

where \( r(z) \) = bake time and \( K(T) \) = cross-linking rate constant (as a function of the bake temperature \( T \)). The temperature dependence of the rate constant is given by the Arrhenius equation

\[
K(T) = A_r \exp\left(-E_a/(RT)\right)
\]

[14]

where \( A_r \) = the Arrhenius coefficient, \( E_a \) = activation energy, and \( R \) = universal gas constant. Thus, all that is left to do is to determine reasonable values for \( A_r \) and \( E_a \).

Figure 4a shows the experimental data given in Ref. (4) for AZ1350J in 1:1 AZ developer

\[
E_a = 20 \text{ kcal/mol}
\]

\[
A_r = 2.6 \times 10^{13} \text{ min}^{-1}
\]

These values are extremely approximative and are given only as reference. This model for the induction effect is a simple one. More complicated behavior has been observed, requiring more complicated descriptions (6).

When a photoresist is coated on a substrate, the resist adheres to the surface of the substrate. This adhesion is in fact a chemical interaction between the resist resin and the substrate. The amount of adhesion is a qualitative measure of the bonding between resist and substrate. The phenomenon of adhesion is essential for the photore sist to 'resist' etching during subsequent processing steps and during development without lifting or washing away. An interesting and often ignored side effect of this property is a decreased development rate near the resist-substrate interface. One might expect that resin molecules that are bonded in some way to the substrate would be harder to dissolve than bulk resin molecules. Experiments have shown that the last 50 nm or so of resist develop more slowly (5).

The adhesion effect can be empirically described in a fashion similar to the induction effect

\[
\tau(z) = r_\infty (1 - (1 - r_\infty e^{-\beta_2 z}))
\]

[15]

where \( r_\infty \) = development rate at the substrate relative to \( r_\infty \), \( d \) = resist thickness, and \( \beta_2 \) = empirical constant. An appropriate value for \( \beta_2 \) is about 30 \( \mu \text{m}^{-1} \). The value of \( r_\infty \) depends on many factors including resist composition, the use of adhesion promoters, substrate cleanliness, etc., or, in short, all those properties that affect adhesion. Modeling these effects would be difficult at best. Thus, to simplify the situation, a value for \( r_\infty \) of 0.5 will be assumed. The resulting models are, of course, quite approximative. Further studies into the exact nature of these effects should be made.

**Advanced Development Concepts**

The kinetic model given in the previous sections represents a first step in an effort to understand the development process. However, there are still many aspects of development not explained by this simple model. This section will point out a few of the problems with the simple model and give directions where solutions to these problems may be found.

The kinetic analysis used above employs the standard assumption of a surface rate limited reaction, that is, the rate limiting reaction is that of the developer with the photore sist on the surface of the resist. Thus, there is an implicit assumption of a distinct resist/developer boundary, as in Fig. 4a. In all probability, however, there is no distinct boundary, but a continuous 'gel' layer of intermixed developer and resist (Fig. 4b). This can be thought of as a diffusion of developer into the resist to a depth \( \delta \). This approach has been previously described as a membrane model for development (8). One effect of this developer diffusion is a 'predevelopment' of the resist before the imaginary resist/developer boundary reaches that point. Note that the surface-limited assumption is a special case of the diffuse-boundary condition when \( \delta = 0 \).

Before one goes to the trouble of formulating a more rigorous treatment of the development process, there should be some physical motivation for the effort. This motivation comes from observations of the development of standing wave patterns in the photoresist. The simple kinetic model to predict a typical resist profile in the presence of standing waves, the result is a series of extremely sharp and distinct standing wave ridges (Fig. 4). SEM photographs of actual resist profiles, however, show much more rounded ridges. Also, the predicted development time needed to clear through the standing waves is significantly faster than actual development times. Both of these discrepancies can be explained by the 'predevelopment' properties of a diffuse-boundary model. Developer diffuses (or is transported through a surface membrane) under the low exposure standing wave peak. Directly below this peak is a high exposure region with a much faster development rate. At \( \delta \) on the order of the depth of a standing wave peak (~50 nm), developer can begin to work on the higher exposure region and remove this standing wave ridge faster.

Another assumption used in all current models of the development process is that development rate is geometric independent. Development rate is thought to be dependent only on exposure (i.e., PAC concentration). However, one can intuitively discuss the difference between the development of a simple photoresist line and a complex pattern in terms of the simple kinetic model to predict a typical resist profile and a small geometry contact window (i.e., with an aspect ratio approaching 1:1). As the window is being developed, the developer solution within the hole flows less freely than the bulk solution, eventually approaching puddle development conditions. Also, within the contact hole, there is a localized buildup of dissolved photoresist. This results in a lower development rate in the vicinity of the contact window and slower development rates. Further, this effect becomes more pronounced as development proceeds. Thus, small feature-size windows develop more slowly than would be predicted by a simple model.

**Conclusions**

An analytical development rate model has been given which is based on a postulated reaction mechanism. Although experiments giving direct confirmation of the mechanism have not been performed, the ability of the predicted rate equation to reproduce accurately experimental data warrants its use. Previous work on photore sist development modeling has been limited to empirical fits of experimental data (1, 2). The disadvantages of an empirical approach are well known: the conditions under which the model is applicable are limited by the conditions governing the original experimental data, and the empirical model gives little or no physical insight into the development process.

Both of these deficiencies are addressed by the reaction mechanism model proposed above. Variations in prebake conditions can be modeled as a change in \( M_0 \), (3), and new values of \( r_{\max} \) and \( n \) can be determined. The...
temperature dependence of the various parameters can also be predicted using the standard Arrhenius plots to determine activation energies. Physically, the model gives insight into the development process on microscopic and macroscopic levels. The threshold behavior of resist development is well known, but can now be quantified by $m_{TH}$. This parameter, along with the selectivity term $n$, can be used to compare the performance of different resist-developer systems in a meaningful way. For example, the use of a 70°C prebake on AZ1350J, as shown in Table I, was found to give a higher selectivity than a 100°C prebake, making the latter temperature less desirable.

It seems likely that the developer selectivity $n$ is somehow related to the resist contrast $\gamma$. In fact, one can relate the definition of contrast to the proposed kinetic development rate equation and derive an analytical expression relating $\gamma$, $n$, and $m_{TH}$ (see Appendix)

$$\gamma_D = -\frac{2.303 \ln \left( \frac{m_{TH} \ln (m_{TH})}{1 - m_{TH}} \right)}{2}$$

where the subscript $D$ signifies developer contrast for a perfect resist. This equation was derived assuming a constant development rate through the film (i.e., no absorption during exposure) and that the contrast is independent of the development time. Conversely, if one assumes an infinite value of the developer selectivity parameter, $n$, and a nonzero absorption coefficient, $\alpha$, the contrast for a resist of thickness $d$ is given by

$$\gamma_D = -\frac{2.303}{(A m_{TH} + B)d}$$

where $A$ and $B$ are the resist absorption parameters as defined by Dill (1), and the subscript $E$ signifies exposure contrast for a perfect developer. Using these two extreme assumptions, one can estimate the actual contrast by

$$\gamma = \left( \frac{1}{\gamma_D} + \frac{1}{\gamma_E} \right)^{-1}$$

Using the parameters in Table I, the contrast for AZ1350J was calculated and is shown in Table I as the predicted contrast.

The kinetic model, however, is not without its drawbacks. Equation (6) predicts that the development rate is proportional to the developer concentration $D$. Although the general trend is correct, studies have shown that the relationship between development rate and developer concentration is much more complicated than a simple linear function (9). Further studies into the proposed development mechanism should be made.

The models presented in this paper for the induction and adhesion effects are empirical in nature. The induction model is similar to other models in the literature (6), the new element being the dependence of $\tau_1$ on the prebake conditions. The limited data in the literature allowed for rough estimates of the activation energy and Arrhenius coefficient for the prebake-induced induction.
If $T_r$ is the relative thickness remaining after development

$$T_r = 1 - \frac{1}{d} \int_{0}^{t_{dev}} r(m(E)) \, dt \quad [A-2]$$

where $d$ is the initial resist thickness, $t_{dev}$ is the development time, and $r$ is the development rate as a function of exposure energy, $E$. If the resist is assumed to be nonabsorbing, the exposure energy, and thus the development rate, will be constant throughout the resist. Thus, for this special case, Eq. [A-2] becomes

$$T_r = 1 - \frac{r_{dev}}{d} \quad [A-3]$$

Let $r_o$ be the development rate (corresponding to exposure energy $E_o$ and PAC concentration $m_o$), which just removes all of the resist in the allotted development time. Thus,

$$r_o = \frac{d}{t_{dev}} \quad \text{and} \quad T_r = 1 - \frac{r}{r_o} \quad [A-4]$$

In terms of Eq. [11]

$$r_o = r_{max} \frac{(a + 1)(1 - m_o)^a}{a + (1 - m_o)^a} \quad [A-5]$$

where $r_{min}$ has been neglected. Using Eq. [A-5] and [11], Eq. [A-4] becomes

$$T_r = 1 - \left[ 1 + \frac{a}{(1 - m_o)^a} \right] \left[ 1 + \frac{a}{(1 - m)^a} \right] \quad [A-6]$$

As previously stated, the contrast is the negative of the slope of the $T_r$ vs. log ($E$) curve at $E = E_o$. In mathematical form

$$\gamma = -2.303 \frac{d(T_r)}{d(ln E)} \bigg|_{E=E_o} \quad [A-7]$$

The derivative can be expanded as

$$\frac{d(T_r)}{d(ln E)} = \frac{d(T_r)}{dm} \cdot \frac{dm}{d(ln E)} \quad [A-8]$$

The far right derivative can be evaluated knowing the effect of exposure on the PAC concentration

$$m = e^{-Ce^{E}} \quad [A-9]$$

where $C$ is the exposure rate constant. Thus

$$\left. \frac{dm}{d(ln E)} \right|_{m=m_o} = m_o \ln (m_o) \quad [A-10]$$

The middle derivative of Eq. [A-6] can be evaluated using Eq. [A-9]

$$\left. \frac{d(T_r)}{dm} \right|_{m=m_o} = \left[ \frac{an}{1 - m_o} \right] \left[ \frac{1}{\alpha + (1 - m_o)^a} \right] \quad [A-11]$$

Thus

$$\left. \frac{d(T_r)}{d(ln E)} \right|_{E=E_o} = \frac{nm_o \ln (m_o)}{1 - m_o} \left[ \frac{1}{1 + (1 - m_o)^a/\alpha} \right] \quad [A-12]$$

Using the definition of a

$$\frac{d(T_r)}{d(ln E)} \bigg|_{E=E_o} = \frac{nm_o \ln (m_o)}{1 - m_o} \left[ \frac{1}{1 + \left( \frac{1 - m_o}{1 - m_{TH}} \right)^n} \right] \quad [A-13]$$

As was previously stated, $m_o$ is the PAC concentration, which causes the film to be just removed in the allotted development time. Typically, the contrast is independent of the development time over the range of normally used times. Thus, let us arbitrarily pick a development time such that $m_o = m_{TH}$. Using this value, the contrast becomes

$$\gamma_o = -2.303 \frac{n + 1}{2} \left( \frac{m_{TH} \ln (m_{TH})}{1 - m_{TH}} \right) \quad [A-14]$$

where $\alpha$ is the absorption coefficient at the bottom of the resist and $d$ is the resist thickness. Again, the subscript denotes the contrast of the resist for a perfect developer. The absorption coefficient is a function of the PAC concentration by

$$\alpha = Am + B \quad [A-15]$$

where $A$ and $B$ are the resist absorption parameters as defined by Dill (1). For this model, $m$ is the PAC concentration at the bottom of the resist. In the previous analysis, we assumed a value of $m_{TH}$ for the PAC concentration. Thus, to be consistently arbitrary, Eq. [A-15] becomes

$$\gamma_o = \frac{2.303}{(Am_{TH} + B)d} \quad [A-16]$$

REFERENCES