

INTERFACE '95

This paper was published in the proceedings of the
OCG Microlithography Seminar, Interface '95, pp. 217-228.

It is made available as an electronic reprint with permission of
OCG Microelectronic Materials, Inc.

Copyright 1995.

One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper are prohibited.

Lithographic Effects Of Acid Diffusion In Chemically Amplified Resists

by

Chris A. Mack

**FINLE Technologies, Inc.
Austin, TX**

Abstract

Chemically amplified resists are based on the generation of acid during exposure to light, followed by an acid catalyzed reaction during a post-exposure bake which changes the solubility of the photoresist in developer. Acid generation is typically assumed to follow standard first order kinetics. However, polymer or dye absorption followed by electron transfer or fluorescent exposure of the photoacid generator (PAG) will also be examined. Amplification will be modeled as a reaction of the acid with the polymer, first order in polymer reactive sites and of arbitrary order in acid. Another important mechanism to consider is acid loss. There are four common pathways for acid loss: atmospheric base contamination, evaporation of acid from the top of the film, neutralization of the acid at the substrate, and bulk acid quenching. All four mechanisms will be treated in this work. The effects of acid diffusion will be investigated by providing a full solution to the reaction-diffusion system of equations for the kinetics of chemically amplified resists. This reaction-diffusion model will include the possibility of a reaction dependent acid diffusivity.

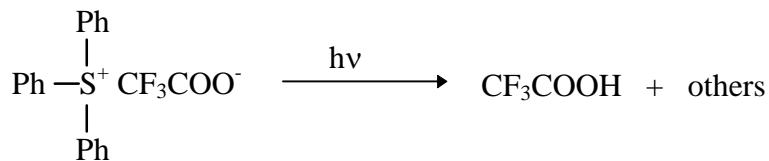
INTRODUCTION

Chemically amplified resists have emerged as the most likely class of resist chemistries for use in Deep-UV lithography. First proposed by Ito and Willson (1), these resists are based on the generation of acid during exposure to light, followed by an acid catalyzed reaction during a post-exposure bake which changes the solubility of the photoresist in developer. For such systems, one molecule of photogenerated acid can cause many (possibly hundreds) of subsequent reactions, thus the name “chemically amplified.” An important aspect of the chemical mechanism of amplification is the diffusion of the acid. This paper will explore the impact of diffusion on the lithographic properties of generic chemically amplified resists using mathematical modeling techniques. The acid generation will be modeled as a first order reaction, and the amplification will have an arbitrary order with respect to the acid concentration.

The diffusion will be modeled with constant diffusivity as well as various forms of reaction dependent diffusivities. The complete system of equations will be solved as a reaction-diffusion system using finite difference techniques. Finally, the solution will be integrated with a complete lithographic modeling program to determine the impact of acid diffusion on lithographic performance.

RESIST KINETICS

The kinetics of the exposure and catalyzed amplification of chemically amplified photoresists have been described elsewhere (2,3), but will be reviewed here for a typical case. These resists are composed of a polymer resin (possibly “blocked” to inhibit dissolution), a photoacid generator (PAG), and possibly a crosslinking agent, dye or other additive. As the name implies, the photoacid generator forms a strong acid, H⁺, when exposed to Deep-UV light. Ito and Willson first proposed the use of an aryl onium salt (1), and triphenylsulfonium salts are now used extensively as PAGs. The reaction of a common PAG is shown below:



The acid generated (trifluoroacetic acid) is a derivative of acetic acid where the electron-drawing properties of the fluorines are used to greatly increase the acidity of the molecule. The PAG is mixed with the polymer resin at a concentration of typically 5-15% by weight, with 10% as a typical formulation.

Sturtevant, et al. (4), describe three possible mechanisms for the photoreaction of the PAG: direct absorption of a photon by the PAG, absorption of a photon by the polymer and subsequent electron transfer to the PAG, and photon absorption by the polymer resulting in fluorescence which then exposes the PAG. For direct photon absorption by the PAG, the kinetics of the reaction would be standard first order:

$$\frac{\partial G}{\partial t} = -CGI \quad (1)$$

where G is the concentration of PAG at time t (the initial PAG concentration is G_o), I is the exposure intensity, and C is the exposure rate constant. For constant intensity, the rate equation can be solved for G :

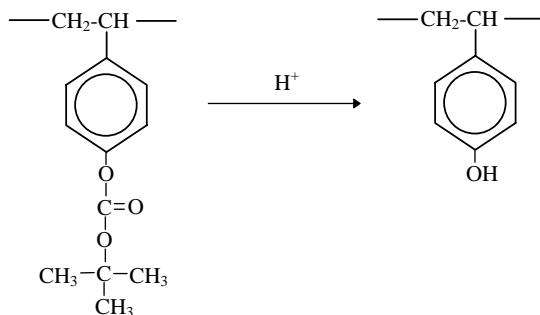
$$G = G_o e^{-CIt} \quad (2)$$

The acid concentration H is given by

$$H = G_o - G = G_o \left(1 - e^{-CIt}\right) \quad (3)$$

The other two non-direct photon absorption mechanisms could lead to different kinetics of exposure. However, for low exposure dose situations, equation (3) and other kinetics leads to near linear response with dose. It is highly likely that a combination of at least two of these mechanisms is occurring in most chemically amplified resists. However, equation (3) should adequately describe the overall dose dependence of acid generation using an effective exposure rate constant C .

Exposure of the resist with an aerial image $I(x)$ results in an acid latent image $H(x)$. A post-exposure bake (PEB) is then used to thermally induce a chemical reaction. This may be the activation of a crosslinking agent for a negative resist or the deblocking of the polymer resin for a positive resist. The reaction is catalyzed by the acid so that the acid is not consumed by the reaction and H remains constant. Ito and Willson first proposed the concept of deblocking a polymer to change its solubility (1). A base polymer such as poly (*p*-hydroxystyrene), PHS, is used which is very soluble in an aqueous base developer. It is the hydroxyl groups which give the PHS its high solubility so by “blocking” these sites (by reacting the hydroxyl group with some non-ionizable groups) the solubility can be reduced. Ito and Willson employed a *t*-butoxycarbonyl group (*t*-BOC), resulting in a very slowly dissolving polymer. In the presence of acid and heat, the *t*-BOC blocked polymer will undergo acidolysis to generate the soluble hydroxyl group, as shown below.



One drawback of this scheme is that the cleaved *t*-BOC is volatile and will evaporate, causing film shrinkage in the exposed areas. Larger molecular weight blocking groups can be used to reduce this film shrinkage to acceptable levels (below 10%). Also, the blocking group is such an effective inhibitor of dissolution, that nearly every blocked site on the polymer must be deblocked in order to obtain significant dissolution. Thus, the photoresist can be made more “sensitive” by only partially blocking the PHS. Typical photoresists use 10-30% of the hydroxyl groups blocked with 20% a typical value. Molecular weights for the PHS run in the range of 3000 to 5000 giving about 20 to 35 hydroxyl groups per molecule.

Using M as the concentration of some reactive site, these sites are consumed (i.e., are reacted) according to kinetics of some unknown order in H and first order in M :

$$\frac{\partial M}{\partial t'} = -K_{\text{amp}} M H^n \quad (4)$$

where K_{amp} is the rate constant of the crosslinking reaction and t' is the bake time. Simple theory would indicate that $n=1$ but the general form will be used here. Assuming H is constant, equation (4) can be solved for the concentration of reacted sites X :

$$X = M_o - M = M_o \left(1 - e^{-K_{amp} H^n t'} \right) \quad (5)$$

(Note: Although H^+ is not consumed by the reaction, the value of H is not locally constant. Diffusion during the PEB causes local changes in the acid concentration, thus requiring the use of a reaction-diffusion system of equations (5). The approximation that H is constant is a useful one, however, which gives insight into the reaction. A more accurate reaction-diffusion approach will be presented in a following section.)

It is useful here to normalize the concentrations to some initial values. This results in a normalized acid concentration h and normalized reacted and unreacted sites x and m :

$$h = \frac{H}{G_o} \quad x = \frac{X}{M_o} \quad m = \frac{M}{M_o} \quad (6)$$

Equations (3) and (5) become

$$\begin{aligned} h &= 1 - e^{-CIt} \\ m &= 1 - x = e^{-\alpha h^n} \end{aligned} \quad (7)$$

where α is a lumped “amplification” constant equal to $G_o^n K_{amp} t'$. The result of the PEB is an amplified latent image $m(x)$, corresponding to an exposed latent image $h(x)$, resulting from the aerial image $I(x)$.

ACID DIFFUSION

The above analysis of the kinetics of the amplification reaction assumed a locally constant concentration of acid H . Although this could be exactly true in some circumstances, it is typically only an approximation and is often a poor approximation. In reality, the acid diffuses during the bake. In one dimension, the standard diffusion equation takes the form

$$\frac{\partial H}{\partial t'} = \frac{\partial}{\partial x} \left(D_H \frac{\partial H}{\partial x} \right) \quad (8)$$

where D_H is the diffusivity of acid in the photoresist. Solving this equation requires a number of things: two boundary conditions, one initial condition, and a knowledge of the diffusivity as a function of position and time.

The initial condition is the initial acid distribution within the film, $H(x,0)$, resulting from the exposure of the PAG. The two boundary conditions are at the top and bottom surface of the photoresist film. The boundary at the wafer surface is assumed to be impermeable, giving a boundary condition of no diffusion into the wafer. The boundary condition at the top of the wafer will depend on the diffusion of acid into the atmosphere above the wafer. Although such acid loss is a distinct possibility, it will not be treated here. Instead, the top surface of the resist will also be assumed to be impermeable.

The solution of equation (8) can now be performed if the diffusivity of the acid in the photoresist is known. Unfortunately, this solution is complicated by two very important factors: the diffusivity is a strong function of temperature and, most probably, the extent of amplification. Since the temperature is changing with time during the bake, the diffusivity will be time dependent. The concentration dependence of diffusivity results from an increase in free volume for typical positive resists: as the amplification reaction proceeds, the polymer blocking group evaporates resulting in a decrease in film thickness but also an increase in free volume. Since the acid concentration is time and position dependent, the diffusivity in equation (8) must be determined as a part of the solution of equation (8) by an iterative method. The resulting simultaneous solution of equations (4) and (8) is called a reaction-diffusion system.

The temperature dependence of the diffusivity can be expressed in a standard Arrhenius form:

$$D_o(T) = A_r \exp(-E_a / RT) \quad (9)$$

where D_o is a general diffusivity, A_r is the Arrhenius coefficient and E_a is the activation energy. A full treatment of the amplification reaction would include a thermal model of the hotplate in order to determine the actual time-temperature history of the wafer (6). To simplify the problem, an ideal temperature distribution will be assumed: the temperature of the resist is zero (low enough for no diffusion or reaction) until the start of the bake, at which time it immediately rises to the final bake temperature, stays constant for the duration of the bake, then instantly falls back to zero.

The concentration dependence of the diffusivity is less obvious. Several authors have proposed and verified the use of different models for the concentration dependence of diffusion within a polymer. Of course, the simplest form (besides a constant diffusivity) would be a linear model. Letting D_o be the diffusivity of acid in completely unreacted resist and D_f the diffusivity of acid in resist which has been completely reacted,

$$D_H = D_o + x(D_f - D_o) \quad (10)$$

Here, diffusivity is expressed as a function of the extent of the amplification reaction. Another common form is the Fujita-Doolittle equation (7) which can be predicted theoretically using free volume arguments. A form of that equation which is convenient for calculations is shown here:

$$D_H = D_o \exp\left(\frac{\alpha x}{1 + \beta x}\right) \quad (11)$$

where α and β are experimentally determined constants and are, in general, temperature dependent. Other concentration relations are also possible (8), but the Fujita-Doolittle expression will be used in this work.

ACID LOSS

Through a variety of mechanisms, acid formed by exposure of the resist film can be lost and thus not contribute to the catalyzed reaction to change the resist solubility. There are two basic types of acid loss: loss that occurs between exposure and post-exposure bake, and loss that occurs during the post-exposure bake.

The first type of loss leads to delay time effects -- the resulting lithography is affected by the delay time between exposure and post-exposure bake. Delay time effects can be very severe and, of course, are very detrimental to the use of such a resist in a manufacturing environment (9,10). The typical mechanism for delay time acid loss is the diffusion of atmospheric base contaminants into the top surface of the resist. The result is a neutralization of the acid near the top of the resist and a corresponding reduced amplification. For a negative resist, the top portion of a line is not insolublized and resist is lost from the top of the line. For a positive resist, the effects are more devastating. Sufficient base contamination can make the top of the resist insoluble, blocking dissolution into the bulk of the resist. In extreme cases, no patterns can be observed after development. Another possible delay time acid loss mechanism is base contamination from the substrate, as has been observed on TiN substrates (10).

The effects of acid loss due to atmospheric base contaminants can be accounted for in a straightforward manner (11). The base diffuses slowly from the top surface of the resist into the bulk. Assuming that the concentration of base contaminant in contact with the top of the resist remains constant, the diffusion equation can be solved for the concentration of base, B , as a function of depth into the resist film:

$$B = B_o \exp(-(z / \sigma)^2) \quad (12)$$

where B_o is the base concentration at the top of the resist film, z is the depth into the resist ($z=0$ at the top of the film) and σ is the diffusion length of the base in resist. The standard assumption of constant diffusivity has been made here so that diffusion length goes as the square root of the delay time.

Since the acid generated by exposure for most resist systems of interest is fairly strong, it is a good approximation to assume that all of the base contaminant will react with acid if there is sufficient acid present. Thus, the acid concentration at the beginning of the PEB, H^* , is related to the acid concentration after exposure, H , by

$$H^* = H - B \quad \text{or} \quad h^* = h - b \quad (13)$$

where the lower case symbols again represent the concentration relative to G_o , the initial photoacid generator concentration.

Acid loss during the PEB could occur by other mechanisms. For example, as the acid diffuses through the polymer, it may encounter sights which “trap” the acid, rendering it unusable for further amplification. If these traps were in much greater abundance than the acid itself (for example, sites on the polymer), the resulting acid loss rate would be first order.

$$\frac{\partial h}{\partial t'} = -K_{loss} h \quad (14)$$

where K_{loss} is the acid loss reaction rate constant. Of course, other more complicated acid loss mechanisms can be proposed, but in the absence of data supporting them, the simple first order loss mechanism will be used here.

Acid can also be lost at the two interfaces of the resist. At the top of the resist, acid can evaporate. The amount of evaporation is a function of the size of the acid and the degree of its interaction with the resist polymer. A small acid (such as the triflic acid discussed above) may have very significant evaporation. A separate rate equation can be written for the rate of evaporation of acid:

$$\left. \frac{\partial h}{\partial t'} \right|_{z=0} = -K_{evap} (h(x,0) - h_{air}(x,0)) \quad (15)$$

where $z = 0$ is the top of the resist and h_{air} is the acid concentration in the atmosphere just above the photoresist surface. Typically, the PEB takes place in a reasonably open environment with enough air flow to eliminate any buildup of evaporated acid above the resist, making $h_{air} = 0$. If K_{evap} is very small, then virtually no evaporation takes place and we say that the top boundary of the resist is impenetrable. If K_{evap} is very large (resulting in evaporation that is much faster than the rate of diffusion), the effect is to bring the surface concentration of acid in the resist to zero.

At the substrate there is also a possible mechanism for acid loss. Substrates containing nitrogen (such as titanium nitride and silicon nitride) often exhibit a foot at the bottom of the resist profile (10). Most likely, the nitrogen acts as a site for trapping acid molecules, which gives a locally diminished acid concentration at the bottom of the resist. This, of course, leads to reduced amplification and a slower development rate, resulting in the resist foot. The kinetics of this substrate acid loss will depend on the concentration of acid trap sites at the substrate, S . It will be more useful to express this concentration relative to the initial concentration of PAG.

$$s = \frac{S}{G_o} \quad (16)$$

A simple trapping mechanism would have one substrate trap site react with one acid molecule.

$$\left. \frac{\partial h}{\partial t'} \right|_{z=D} = -K_{trap} h(x, D) s \quad (17)$$

Of course, the trap sites would be consumed at the same rate as the acid. Thus, knowing the rate constant K_{trap} and the initial relative concentration of substrate trapping sites s_0 , one can include equation (17) in the overall mechanism of acid loss.

REACTION-DIFFUSION SYSTEM

The combination of a reacting system and a diffusing system where the diffusivity is dependent on the extent of reaction is called a reaction-diffusion system. The solution of such a system is the simultaneous solution of equations (4) and (8) using equation (3) as an initial condition and equation (10) or (11) to describe the reaction-dependent diffusivity. Of course, any or all of the acid loss mechanisms can also be included. A convenient and straightforward method to solve such equations is the finite difference method (see, for example, reference 12). The equations are solved by approximating the differential equations by difference equations. By marching through time and solving for all space at each time step, the final solution is the result after the final time step. A key part of an accurate solution is the choice of a sufficiently small time step. If the spatial dimension of interest is Δx (or Δy or Δz), the time step should be chosen such that the diffusion length is less than Δx . For the calculations that follow, the time step was adjusted so that the maximum possible diffusion length during one time step was one third of the spatial increment Δx .

MODELING RESULTS

The reaction-diffusion system described above was integrated into the comprehensive lithography simulation program PROLITH/2 (13), including atmospheric base contamination and bulk acid loss. This software package predicts the light distribution within the resist during exposure by a projection optical system, solves the exposure rate equation (including the possibility of a film whose optical properties change during exposure), uses a 2-dimensional version of the reaction-diffusion solution described above, and then models the development as a function of the extent of amplification to produce a two-dimensional cross-section of a photoresist profile.

Using PROLITH/2 to predict lithographic results such as a resist linewidth or the dose-to-clear (E_o) provides a mechanism for exploring the effects of different diffusion properties. Figure 1 shows a simulation of the dose-to-clear as a function of the acid diffusivity assuming a constant diffusivity and a post-exposure bake time of 60 sec and using the modeling parameters given in Table I. The simulation used a silicon wafer substrate resulting in significant standing waves within the resist. As a result, a minimum amount of diffusion is required for the development process to punch through the standing waves and clear to the bottom of the resist. A diffusivity of about $10 \text{ nm}^2/\text{s}$ (corresponding to a diffusion length of 35 nm) is needed to eliminate the effects of standing waves on E_o .

Figure 2 shows how linewidth and sidewall angle of the photoresist profile are influenced by diffusivity. As both plots indicate, a minimum diffusivity is required to reduce the standing waves in order to obtain reasonable lithographic results. The resist profile simulations also show that excessive diffusion results in poor lithographic performance. As the diffusivity increases, the latent image in the resist begins to degrade, causing in this case an increase in the linewidth (as measured at the bottom of the profile) and a reduction of the sidewall angle.

From Figure 2 one could conclude that a diffusivity of about $15 \text{ nm}^2/\text{s}$ to about $40 \text{ nm}^2/\text{s}$ is required to give acceptable results. Confirmation of this range can be obtained by examining the effect of diffusion on process latitude. Figure 3 shows two focus-exposure matrices for diffusivities of $20 \text{ nm}^2/\text{s}$ and $50 \text{ nm}^2/\text{s}$ (corresponding to diffusion lengths of 49 and 69 nm, respectively). A loss of focus and exposure latitude is observed for the larger diffusion.

CONCLUSIONS

From the above simulation results, it is quite apparent that diffusion plays an important role in the lithographic behavior of chemically amplified resists. A minimum amount of diffusion is required to reduce the effects of standing waves. However, too much diffusion results in a degradation in the latent image and thus reduced lithographic performance. For the case of a constant diffusivity, diffusion lengths between 40 and 70 nm are required to meet the competing demands. If, however, the diffusivity is not constant, more latitude and improved performance can be obtained. What is required is an increase in the diffusivity as a function of the extent of reaction. The areas which are to be dissolved in the developer (the exposed areas of the positive resist) should have a high diffusivity to remove standing waves. The unexposed areas should have a low diffusivity to limit the degradation of the latent image. An ideal resist would have a diffusivity tailored to create a "diffusion well" in the exposed areas, which will not allow the diffusion of acid into the unexposed areas.

ACKNOWLEDGMENTS

The author would like to thank Jeff Byers and John Sturtevant of SEMATECH, and John Petersen of Shipley Co. for many useful and enlightening discussions on chemically amplified resists.

REFERENCES

1. H. Ito and C. G. Willson, "Applications of Photoinitiators to the Design of Resists for Semiconductor Manufacturing," in Polymers in Electronics, ACS Symposium Series 242 (1994) pp. 11-23.
2. R. A. Ferguson, J. M. Hutchinson, C. A. Spense, and A. R. Neureuther, *J. Vac. Sci. Technol. B* 8, 1423 (1990).

3. D. Ziger, C. A. Mack, and R. Distasio, Proc. SPIE **1466**, 270 (1991).
4. J. Sturtevant, S. Holmes, W. Conely, R. Bantu, W. Brunsvold, J. Byers, and S. Webber, "The Role of Photosensitization in DUV Resist Formulations," *SPE 10th International Conference on Photopolymers, Proc.*, (1994).
5. E. Barouch, U. Hollerbach, S. A. Orszag, M. T. Allen, and G. S. Calabrese, Proc. SPIE **1463**, 336 (1991).
6. C. A. Mack, D. P. DeWitt, B. K. Tsai, and G. Yetter, "Modeling of Solvent Evaporation Effects for Hot Plate Baking of Photoresist," *Advances in Resist Technology and Processing XI, Proc.*, SPIE Vol. 2195 (1994) pp. 584-595.
7. H. Fujita, A. Kishimoto, and K. Matsumoto, "Concentration and Temperature Dependence of Diffusion Coefficients for Systems Polymethyl Acrylate and n-Alkyl Acetates," *Transactions of the Faraday Society*, Vol. 56 (1960) pp. 424-437.
8. D. E. Bornside, C. W. Macosko and L. E. Scriven, "Spin Coating of a PMMA/Chlorobenzene Solution," *Journal of the Electrochemical Society*, Vol. 138, No. 1 (Jan., 1991) pp. 317-320.
9. S. A. MacDonald, et al., "Airborne Chemical Contamination of a Chemically Amplified Resist," *Advances in Resist Technology and Processing VIII, Proc.*, SPIE Vol. 1466 (1991) pp. 2-12.
10. K. R. Dean and R. A. Carpio, "Contamination of Positive Deep-UV Photoresists," *OCG Microlithography Seminar Interface '94, Proc.*, (1994) pp. 199-212.
11. T. Ohfuji, A. G. Timko, O. Nalamasu, and D. R. Stone, "Dissolution Rate Modeling of a Chemically Amplified Positive Resist," *Advances in Resist Technology and Processing X, Proc.*, SPIE Vol. 1925 (1993) pp. 213-226.
12. F. P. Incropera and D. P. DeWitt, Fundamentals of Heat and Mass Transfer, 3rd edition, John Wiley & Sons (New York: 1990).
13. FINLE Technologies, Austin, Texas
14. Jeff Byers, private communication.

Table I. Typical PROLITH/2 input parameters for simulation of chemically amplified resists

Imaging Tool:	CEL or Top ARC:
Wavelength = 248.0 nm	Not Used
Bandwidth = 0.0 nm	Intermediate Layers: none
Numerical Aperture = 0.6	Substrate: Silicon
Reduction Ratio = 4.0	
Image Flare = 0.00	Resist System: Positive
Aberrations: None	Thickness = 0.800 μm
Partial Coherence = 0.50	Absorption Parameter A = -0.10 1/ μm
Linewidth = 0.25 μm	Absorption Parameter B = 0.30 1/ μm
Pitch = 0.50 μm	Exposure Rate Const. C = 0.01 cm^2/mJ
Mask Bias = 0.0 μm	Refractive Index = 1.75
Focal Position = -0.20 μm	Development Model: Original Mack
Exposure Energy = 25.0 mJ/cm^2	Max Develop Rate = 100.0 nm/s
Chem. Amp. PEB Parameters	Min Develop Rate = 0.05 nm/s
PEB Bake Time = 60.0 sec	Threshold M = -100.
Acid Reaction Order = 1	Selectivity Parameter n = 5.00
Amplification Rate Const. = 0.10 s^{-1}	Relative Surface Rate = 0.10
Acid Loss Rate Constant = 0.010 s^{-1}	Inhibition Depth = 0.10 μm
Atmospheric Contamination: None	Development Time = 60.0 sec

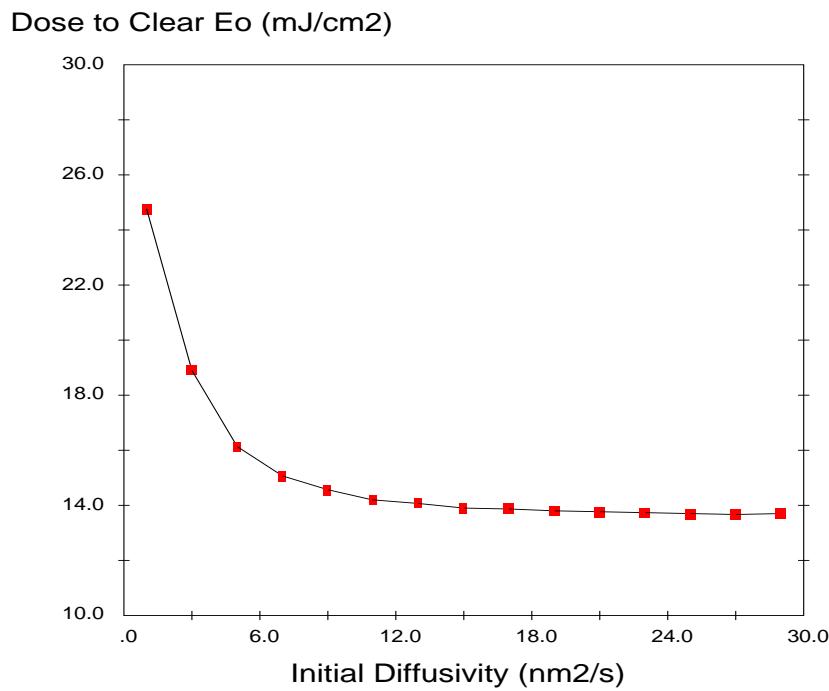


Figure 1. Assuming constant diffusivity for a 60 second post-exposure bake, a simulation of dose-to-clear versus acid diffusivity shows that a minimum amount of diffusion is required for the development process to punch through the standing waves (14).

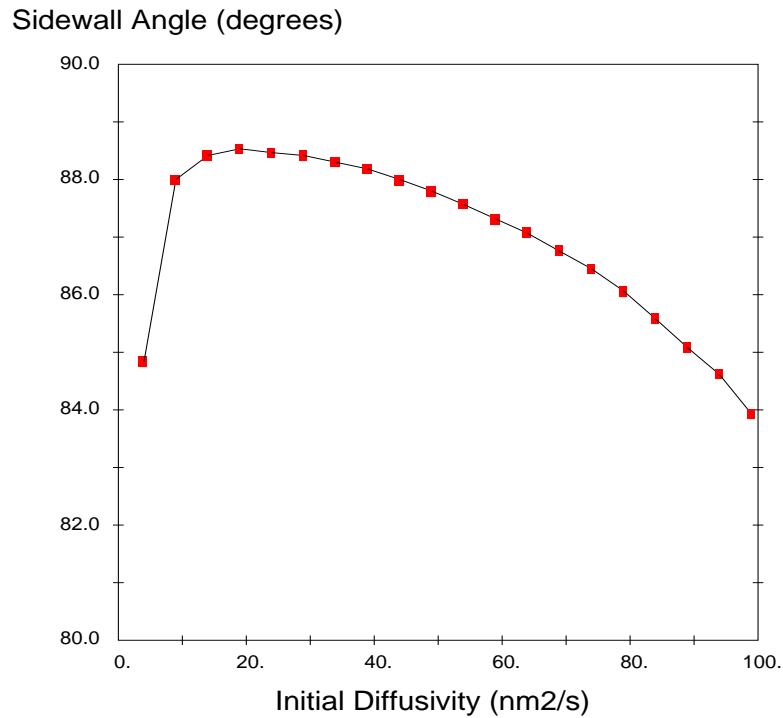
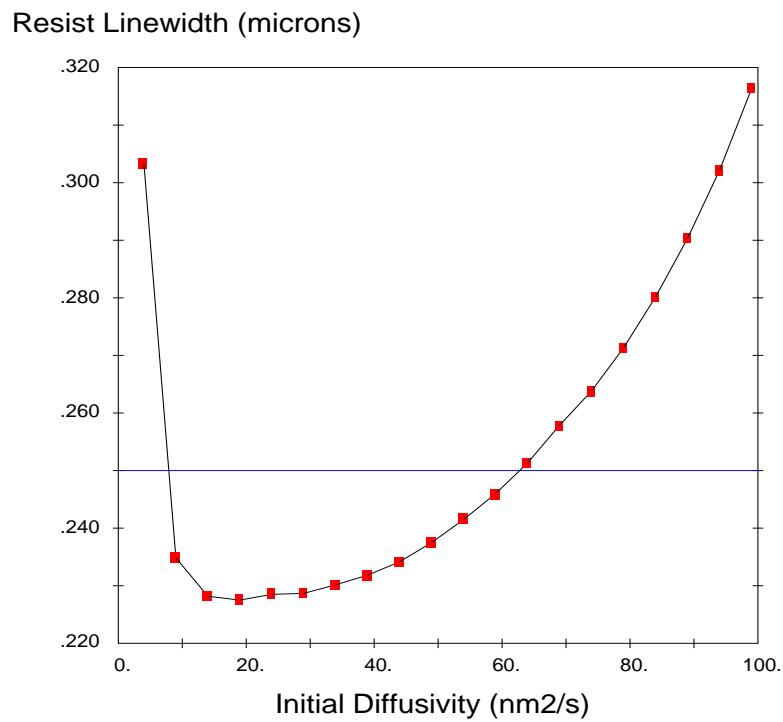
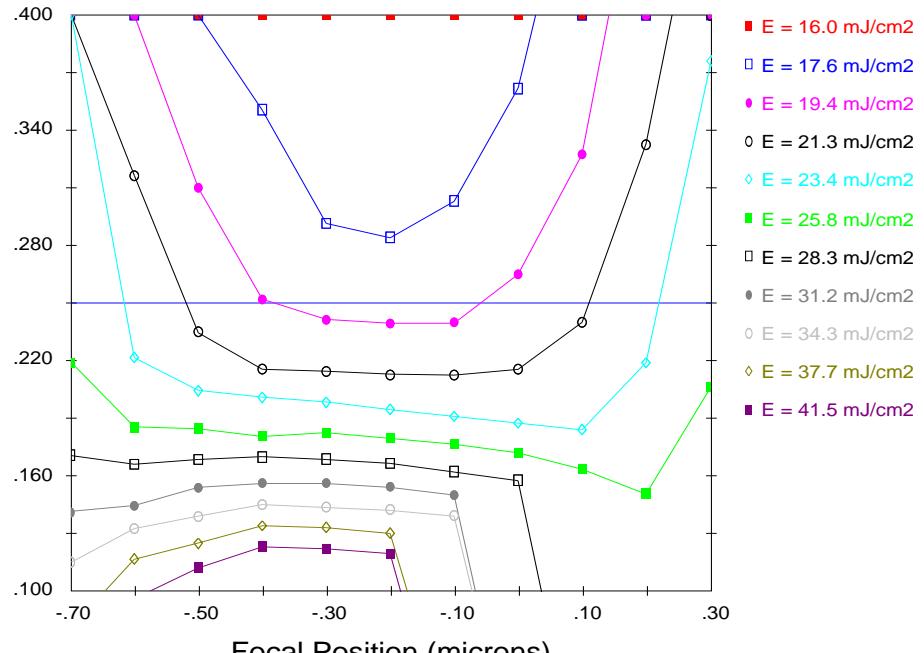


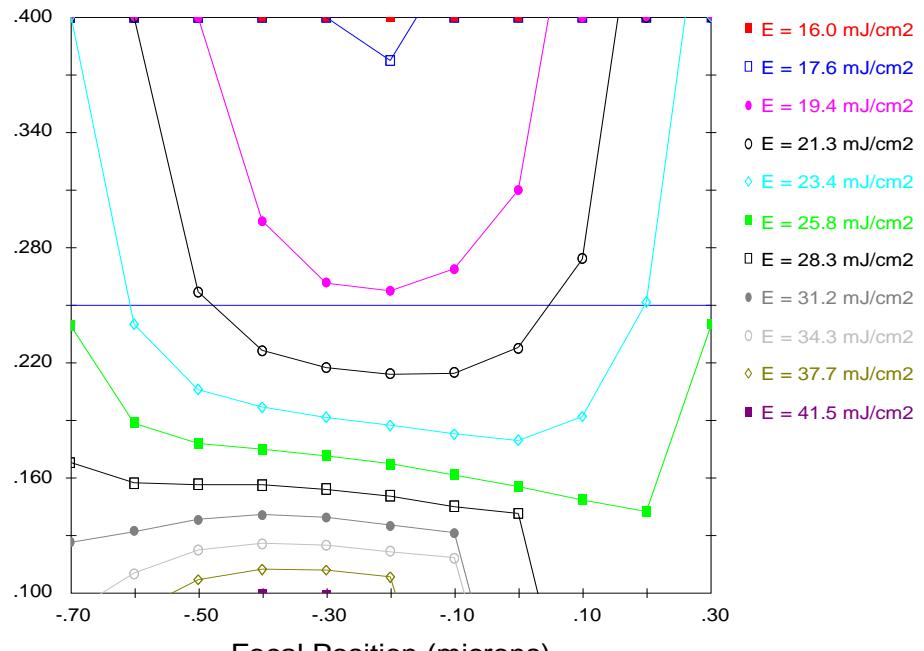
Figure 2. Effect of a constant diffusivity (60 second PEB) on resist linewidth and sidewall angle.

Resist Linewidth (microns)



(a)

Resist Linewidth (microns)



(b)

Figure 3. Focus-exposure matrices showing the effect of diffusivity on process latitude for (a) $20 \text{ nm}^2/\text{s}$ and (b) $50 \text{ nm}^2/\text{s}$ constant diffusivities and a 60 second PEB.