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Calibration of Chemically Amplified Resist Models

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Introduction:

Chemically amplified (CA) resists are expected to provide the majority of the lithography capability for 0.25 micron feature sizes. The sensitivity of CA resists to processing conditions makes implementation of a resist system very dependent on the tool set (stepper, track etc.) used. Modeling of these systems can be useful in optimizing a process for a particular tool set. However, the modeling parameters are also sensitive to the target tool set. Variations in dose calibration between different steppers, the differing temperature ramps found in contact and proximity bakes, and batch to batch variations between resist materials are examples why resist model parameters require calibration to each tool set.

An ideal calibration procedure would entail in-situ measurement techniques at each processing step. The techniques would analytically determine chemical, physical, and kinetic quantities relevant to the resist system and processing conditions. Methods previously used have included interferometric measurement of photobleaching, FTIR measurement of the deprotection extent^{1,2}, in-situ DRM measurements³, etc. Unfortunately, few if any fabs are equipped with the necessary in-situ techniques for complete model calibration.

Methodology:

If the basic assumption is made that the resist develop rate depends only upon the final deprotection extent and not on the processing path,⁴ then the resist exposure and PEB model parameters can be extracted from measurements of resist develop rate across a matrix of processing conditions.⁵ Furthermore, the thickness remaining after a given develop time is related to the integrated develop rate through depth into the resist. Hence, exposure PEB and develop rate model parameters extraction should in principle be possible from resist contrast curves. This method of parameter extraction has been referred to as the poor man's DRM method.⁶

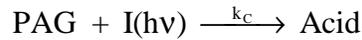
Without any z dependence in the development of open field exposures the develop rate would be simply the thickness change per develop time. However, resist absorbance, standing waves and surface inhibition all necessitate using a 1-d simulation to extract model parameters from contrast curves. In this work a 1-d simulation of the chemically amplified resist system was coupled with a fitting procedure to minimize the least-squares error between observed and model predicted contrast curves. The details of the model are described below. The fitting program used the Levenberg-Marquardt⁷ nonlinear least-squares algorithm. Because of the convergence possibility of the Levenberg-Marquardt algorithm into localized minima, the least-squares fit was

performed from a large set of random guesses of initial parameters. The best set of solutions was then chosen as the final answer.

The procedure was taken one step further and an attempt to calibrate model parameters simple from sitting the dose-to-clear exposures from the same set of contrast curves was made. The fitting program was modified to accept E_0 vs processing conditions and then optimize the model parameters in a least-squares sense.

Exposure model:

The resist exposure step is modeled as a first-order reaction of a Photoacid generator (PAG) with the exposing light.



The resulting concentration of Photoacid as a function of exposure dose is

$$[\text{Acid}]_{\text{Dose}} = [\text{PAG}]_0 \cdot (1 - e^{-k_c \cdot \text{Dose}}) \quad (1)$$

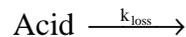
where $[\text{PAG}]_0$ is the initial concentration of PAG in the resist. The z dependence of the exposure dose was modeled using simplified form of the full wave equation result.⁸

$$\text{Dose}(z) = \text{Dose}(0) * \left(e^{-\alpha z} + |r|^2 e^{-\alpha(2d-z)} - 2|r|e^{-\alpha d} \cos\left(\frac{4\pi n}{\lambda}(d-z)\right) \right) \quad (2)$$

In equation (2) α is the linear absorbance of the resist film, d is the film thickness, n is the real part of the refractive index, λ is the exposure wavelength and r is the reflectivity coefficient of the resist/substrate interface. Dose(0) is the applied dose corrected by the reflectivity of the air/resist surface.

Post-Exposure Bake model:

For the post-exposure bake process, the previously reported acid catalyzed deprotection reaction with first order acid loss reaction was used.^{9,10} The acid catalyzed deprotection reaction was slightly modified to include a diffusion controlled association between the reactants followed by the deprotection reaction.



This modification was implemented to model systems where both diffusion and deprotection can limit the overall deprotection rate at different PEB temperatures. The equations which model the PEB are then

$$\frac{d[M]}{dt} = -\frac{\sigma D \cdot k_a}{\sigma D + k_a} \cdot [\text{Acid}] \cdot [M] \quad (3)$$

and

$$\frac{d[\text{Acid}]}{dt} = -k_{\text{loss}} \cdot [\text{Acid}] + D \nabla^2 [\text{Acid}] \quad (4)$$

The PEB model equations were solved numerically given the initial conditions of equal distribution of protecting groups and z dependence of the acid catalyst from the exposure model.

The temperature dependence of the rate constants k_{loss} and k_a were modeled using standard Arrhenius equations

$$k_{\text{loss}} = A_{\text{loss}} e^{\frac{-E_{\text{loss}}}{RT}} \quad (5)$$

$$k_a = A_a e^{\frac{-E_a}{RT}} \quad (6)$$

The temperature dependence of the diffusion coefficient was modeled using a Williams-Landau-Ferry¹¹ modification of the Fujita-Doolittle equation.

$$D = RT A_d e^{\frac{-B_d}{V_f}} \quad (7)$$

where V_f is the free volume of the resist, A_d is a constant dependent upon the size and shape of the diffusing molecule and B_d is a constant which quantifies the ability of the diffusant to use the available free volume. Through thermal expansion the free volume of the resist varies with temperature

$$V_f = V_g + \alpha(T - T_g) \quad (8)$$

where T_g is the glass transition temperature of the resist matrix, V_g is the available free volume at T_g , and α is the thermal expansion coefficient which differs above and below T_g . Other factors besides Temperature can affect the free volume for diffusion. Remaining solvent, deprotection reaction products and the photoacid itself all add to the free volume and hence the diffusivity of the photoacid.^{5,10}

Develop Model:

The develop step was modeled using a surface limited development dependent upon the extent of deprotection. The standard Mack develop rate was chosen as the model function.

$$R(m) = R_{\max} \cdot \frac{(a+1) \cdot (1-m)^n}{a + (1-m)^n} + R_{\min} \quad (9)$$

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

The develop rate at each depth into the resist, $R(z)$, was calculated using equation 9 and the PEB modeled deprotection extent. The thickness of resist remaining after a fixed develop time was then calculated as output from the 1-d simulation. For E_0 modeling, a bisection search algorithm was used to determine the exposure at which the time-to-clear exactly matched the develop time.

APEX/e Results:

APEX/e is the most commonly used resist for DUV applications. It is also the most studied resist for DUV models. The relevant resist parameters for modeling the DUV process at SEMATECH have previously been extracted using a variety of techniques combined, including in-situ DRM tool, ellipsometry measurements, in-situ FTIR and adjustments to fit actual lithography images. These parameters are given in Table I.

Table I APEX/e Resist Model Parameters Set for SEMATECH DUV Process.

$n_{248\text{nm}}$	1.746
$\alpha_{248\text{nm}}$	0.47 $1/\mu\text{m}$
k_c	0.012
E_a	32 mJ/cm^2
$\ln(A_a)$	42.45
E_{loss}	15 mJ/cm^2
$\ln(A_{\text{loss}})$	16.18
E_d	30 mJ/cm^2
$\ln(A_d)$	45.13
R_{\max}	130nm/s
R_{\min}	0.4nm/s
R_n	5.1
R_{mth}	0.34

Calibration of this model on a different tool set was first tried using a 90C PEB process and the simple E_0 approach. The tool set included an SVG90 series track linked to a Micrascan II stepper. Twenty-five wafers with exposure matrices of 0.5 mJ/cm^2 increments were processed at various PEB and develop times. The dose to clear was extracted from the wafers and are listed in Table II. The entire set of resist parameters were adjusted to minimize the least-squares error between model and experiment.

Table II. Dose-to-Clear (mJ/cm^2) as a function of Develop and PEB time for APEX/e, PEB @90C, Micrascan II exposure tool.

PEB Time	Develop Time (s)				
	9	14	24	44	84
30	9.23	8.04	5.98	5.16	4.69
45	5.57	4.8	4.2	3.63	2.9
60	4.38	3.8	3.28	2.86	2.4
90	3.25	3.0	2.6	2.12	1.9
120	2.74	2.56	2.15	2.02	1.6

It was found that many different parameter sets would yield acceptable model predicted E_0 's. Yet, simulation results from several of these parameters sets show different dose to size and resist profiles. Because with each wafer we are using only one experimental data point (E_0), the number of resist parameters that can be effectively calibrated is limited. Particularly, the averaged development rate for which data is available in these E_0 points is limited to equal 10nm/s (800nm thickness/80s develop time). The resist profiles eventually size in regions in which the develop rate is less than 10nm/s so any effective model must fit this region.

Therefore full contrast curve including all the exposures below and including the E_0 point was next used for the calibration procedure. The number of acceptable parameters sets was greatly reduced and all were relatively close to each other in parameter values and resulting simulation results.

The best solution set was chosen as the base set for this particular tool set. The calibration from E_0 points was performed again while fixing various parameters to the base set. It was found that either the develop parameters or the set of $\{k_c, k_a \text{ and } k_{\text{loss}}\}$ could be calibrated using only the E_0 points. However, both could not be calibrated at the same time.

Figure 1 shows the results of calibration, while fixing the develop rate parameters to the base set. Finally, the focus-exposure matrix for APEX/E resist on this target tool set was measured experimentally and simulated using the base set of parameters and PROLITH/2. The comparison to experiment is shown in figure 2. For simulation the exposure tool parameters NA, σ and flare were set to .6,.5, and .08 respectively. The k_c parameter was reduced by 8% to correct for the flare amount in the exposure tool which wasn't included in the 1-d simulations for parameter calibration .

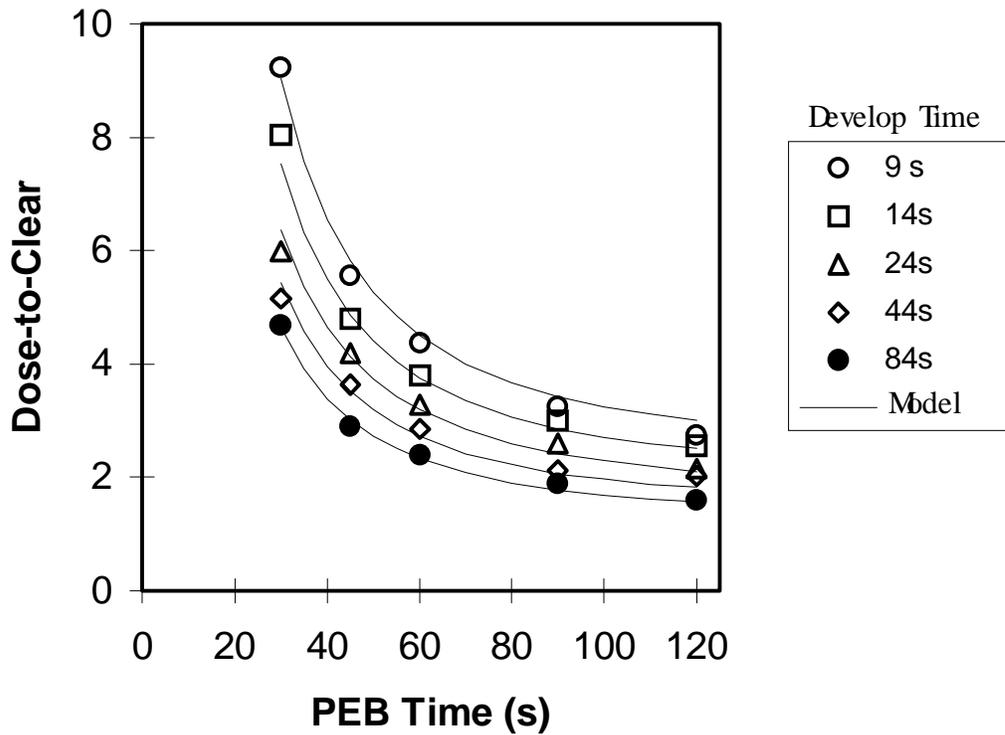


Figure 1. Dose-to-Clear versus PEB time for various develop times, comparison of experimental and model converged fit.

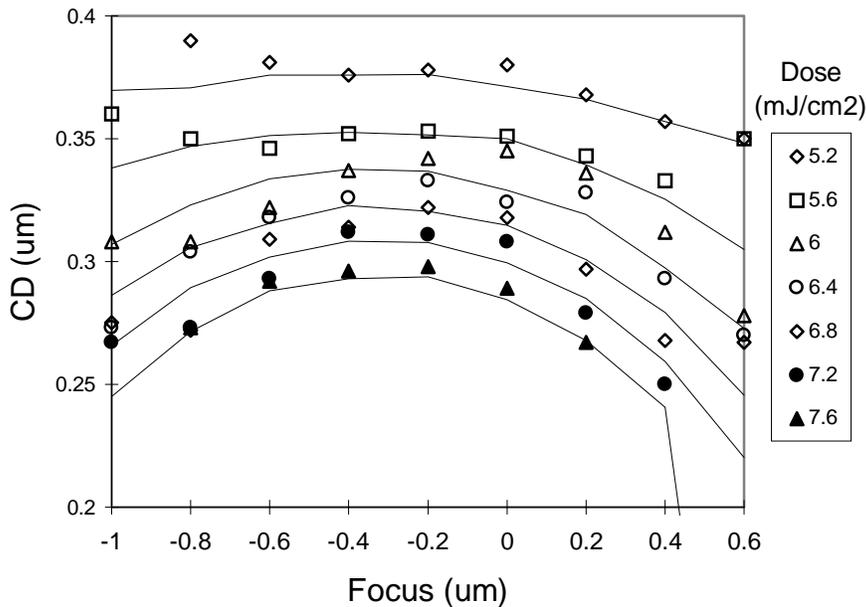


Figure 2. Focus-Exposure matrix for APEX/e 0.347 μ m lines (1.0 μ m pitch) on silicon. Micrascan II exposure tool, PEB @90C. Comparison with PROLITH/2 simulation (solid lines) using calibrated parameters.

Conclusions:

It is possible to calibrate a chemically amplified resist model to a particular tool set using a film thickness measurement tool and running open frame exposure matrices for various processing conditions. The resist loss during development can be used to converge the resist model parameters using an iterative fitting procedure. This method is relatively fast and cost effective per calibration and does not require access to more sophisticated measuring techniques.

The large number of fitting parameters results in somewhat non-uniqueness of solutions across a limited processing space. As a result, convergence of a solution to experimental result does not confirm physical relevance of a proposed model.

The E_0 method can be used to calibrate only a small number of resist parameters simultaneously. However, this method is especially effective for calibrating k_c , k_a and k_{loss} when development parameters are fixed.

The use of many contrast curves or the Poor Man's DRM method can be used for calibrating a larger number of parameters. The larger number of data points from the partially cleared resist thickness provides access to the lithographically relevant regions of the develop rate curve not accessible to the simple E_0 procedure.

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