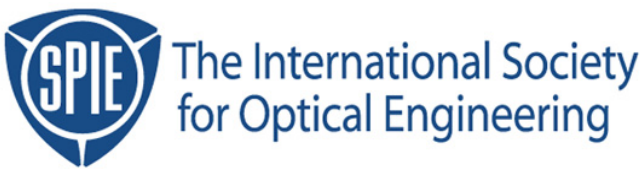


This paper was published in the proceedings of
Advances in Resist Technology and Processing XVI,
SPIE Vol. 3678, pp. 1001-1011.
It is made available as an electronic reprint with permission of SPIE.

Effect of Developer Temperature and Normality On Chemically Amplified Photoresist Dissolution

Mark John Maslow[1], Chris A. Mack[1], Jeffrey Byers[2]

[1]FINLE Technologies Inc., P.O. Box 162712, Austin TX, 78716
[2]International SEMATECH, 2706 Montopolis Dr., Austin, TX 78741
email: Mark_Maslow@FINLE.COM

ABSTRACT

The effects of developer temperature and developer normality on the dissolution behavior of a 248nm chemically amplified resist are examined using development rate measurements. Using an RDA-790 development rate measurement tool employing a 470nm Blue LED measurement wavelength, dissolution rates as a function of dose and depth into the resist were measured. Each data set was analyzed and the performance of rate versus t-BOC concentration was fit to appropriate models. The variation of these results with developer temperature has led to further temperature-dependent characterization of the dissolution modeling parameters. The variation of dissolution rate with developer normality has led to an initial characterization of the normality-dependent dissolution modeling parameters. The maximum dissolution rate R_{max} is shown to exhibit two regions of Arrhenius behavior with a well defined activation energy for both. The dissolution selectivity parameter *n* proves to have a more complicated behavior.

Keywords: Photoresist Development, Developer Temperature, Developer Normality, CA-Resists, Lithography Simulation, PROLITH

1. INTRODUCTION

It has been shown previously that there is significant impact of developer temperature on resist performance [1]. The previous work has produced a well-understood model for the behavior of the temperature dependence of conventional photoresist dissolution rate. As the industry continues to advance chemically amplified resist technology, the behavior of these new resists under varying developer temperatures and developer normalities is less understood.

This paper will analyze the effects of developer temperature and developer normality on the dissolution rate of Shipley APEX-E chemically amplified resist. Using the RDA-790 development rate monitor [2,3], dissolution rate as a function of dose and depth into resist was measured. Each data set was analyzed and the basic performance of dissolution rate versus extent of amplification reaction was fit to mathematical models. The variation of the dissolution rate with developer temperature and developer normality has lead to an initial temperature-dependent, normality-dependent characterization of dissolution modeling parameters for APEX-E chemically amplified resist.

Once models have been established for the temperature and normality dependence of the dissolution behavior, comprehensive simulated experiments, not practical in a laboratory setting, can be performed. The results will lead to improved models that allow the optimization of developer temperature and developer normality for advanced sub-0.25μm processes.

2. THEORY

The dissolution rate of a photoresist as a function of exposure dose is often characterized by fitting the response to a model. If the model adequately describes the shape of the actual data, the parameters of the model will provide a compact representation of the dissolution rate behavior. For example, the dissolution rate of a photoresist, *R*, as a function of the relative photoactive compound (PAC) concentration, *m*, can often be fit well with the four-parameter Mack kinetic model [4]:

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

where R_{max} is the maximum (fully exposed) dissolution rate, R_{min} is the minimum (unexposed) dissolution rate, n is the dissolution selectivity (which corresponds to the surface reaction order), and a is a simplifying constant given by

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

and where m_{TH} is the threshold PAC concentration, defined as the point of inflection of the *R(m)* curve. Here, unexposed resist dissolution (given by R_{min}) is assumed to occur by a separate mechanism from exposed dissolution. In some cases, m_{TH} takes on a large negative value and a becomes large. In this case, the dissolution model simplifies to

$$R = R_{\max}(1-m)^n + R_{\min} \tag{2}$$

Other models are also possible, such as the enhanced kinetic model proposed by Mack [5] and the "notch" model of Mack and Arthur [6]. The notch model is especially effective in describing many of today's most advanced resists. This notch model begins with the simple version of the Mack model given in equation (2) and adds a notch function equivalent to the threshold behavior given by equation (1).

$$R = R_{\max}(1-m)^n\left[\frac{(a+1)(1-m)^{n\_notch}}{a+(1-m)^{n\_notch}}\right] + R_{\min} \tag{3}$$

where

$$a = R_{\max}\frac{(n\_notch+1)}{(n\_notch-1)}(1-m_{TH\_notch})^{n\_notch}$$

The term in the brackets of equation (3) provides the notch-like behavior where m_{TH_notch} is the position of the notch along the PAC concentration axis and *n_notch* gives the strength of the notch. Note that the five parameter notch model of equation (3) reverts to the original Mack model of equation (1) when $n = 0$ and becomes equivalent to the simplified Mack model of equation (2) when $n\_notch = 1$.

The effect of temperature on dissolution rate has been studied previously [1]. The results show a complicated behavior where changes in developer temperature produce changes in dissolution rate that are dose dependent. Thus, at one dose the effect of temperature on dissolution rate can be very different than at another dose. Use of a dissolution rate model can simplify the description of temperature and normality effects by showing just the change in the model parameters with the developer temperature and normality.

3. EXPERIMENTAL

APEX-E was measured using an RDA-790 resist development analyzer manufactured by Litho Tech Japan. The system uses a measurement head with 18 channels of 470nm wavelength signals to provide reflectance interferometry on 18 exposure sites on the wafer simultaneously. The resulting reflectance versus time signals are converted to resist thickness versus time and finally development rate versus thickness using the tool's built-in LEAPSET software. The RDA-790 is equipped with a NESLAB RTE-111 constant temperature bath that provides better than 0.02ºC control of the developer temperature for immersion-mode (agitated with a magnetic stirrer) dissolution rate measurements. Developer can be pumped directly into the immersion tank or can be hand-poured.

Application, exposure, and PEB of the resist was performed using SEMATECH's standard process flow for APEX-E (see Table I) with the wafers going through PEB immediately following exposure. The exposure dose ranged from 2 - 20 mJ/cm^2. Resist dissolution was measured in Shipley CD-26 developer at temperatures from 5ºC to 45ºC in 5ºC increments. CD-26 was diluted to run at normalities from 0.13 to 0.26. The data was then analyzed in the ProDRM [7] software package to convert the rate versus dose and depth in the resist, *R(E,z)*, into rate versus relative PAC concentration (or in this case, t-BOC concentration), *R(m)*, and then fit to a development model. The original Mack model of equation (1) was found to give good fits at all temperatures and normalities.

Table I. APEX-E Processing Conditions

Resist Thickness	~8KÅ on Silicon
Softbake Temperature	90 ºC
Softbake Time	60 sec
Stepper	Ultratech 7200 XLS
Stepper NA	0.53
Stepper Illumination	Annulus, 0.74/0.54
PEB Temperature	90 ºC
PEB Time	60 sec
Wafer Track	SVG 90s Series

4. RESULTS

4 - 1. Developer Temperature Effects

All data collected for the developer temperature study used Shipley CD-26 developer at 0.26N. The variation of the dissolution behavior with developer temperature was similar to previously studied I-line resists [1]. These previously studied resists showed a negative m_{TH} value allowing use of the simplified model in equation (2). APEX-E exhibited a positive m_{TH} value, shown to have a small dependence on the developer temperature. The overall behavior of APEX-E is illustrated in Figures 1-3.

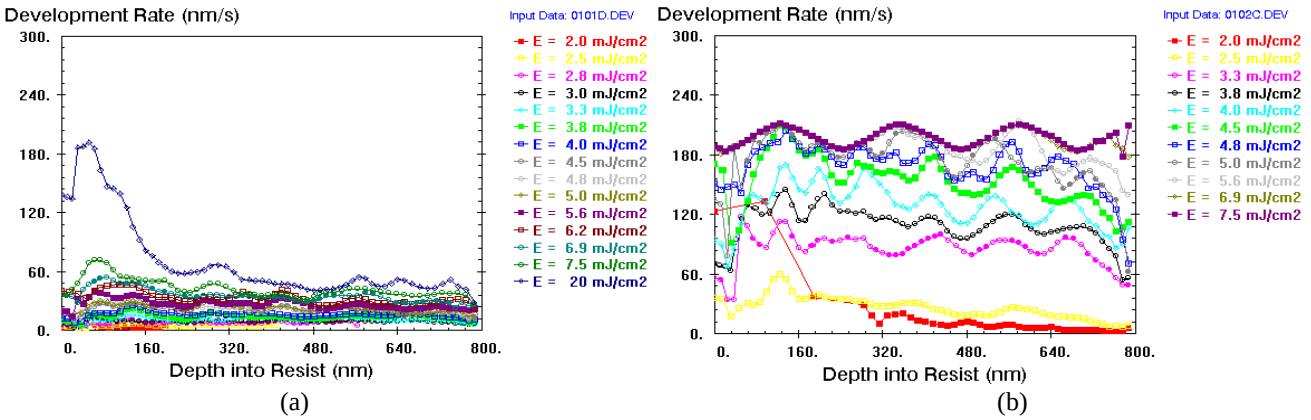


Figure 1: Dissolution rate data from the RDA-790 for APEX-E at developer temperatures (a) 5ºC, and (b) 45ºC.

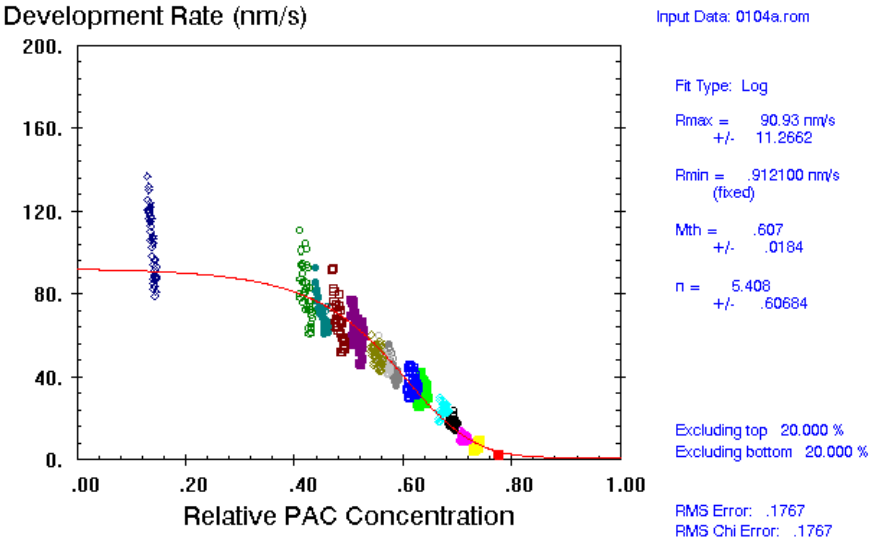


Figure 2: Plot showing the dissolution rate as a function of relative PAC concentration at 35ºC developer temperature, 0.24425 N overlaid with the best fit to the original Mack development rate model.

In fitting the dissolution behavior to a development model, the variation of the *R(m)* curve with temperature can be shown as in Figure 4. For this fitting, the top and bottom 20% of the resist was excluded in order to eliminate surface and substrate effects. This analysis of the bulk development behavior shows that as temperature increases, the maximum development rate (R_{max}) increases. The increase is independent of the exposure dose for higher exposure energies. At lower doses (higher concentrations of PAC) a shift in the threshold PAC concentration m_{TH} and an increase in the dissolution parameter n result in more complicated dissolution rate behavior. Measuring R_{min} without including surface effects requires considerable care and was not attempted in this work. Simple R_{min} calculations were performed on unexposed sites measured before and after development.

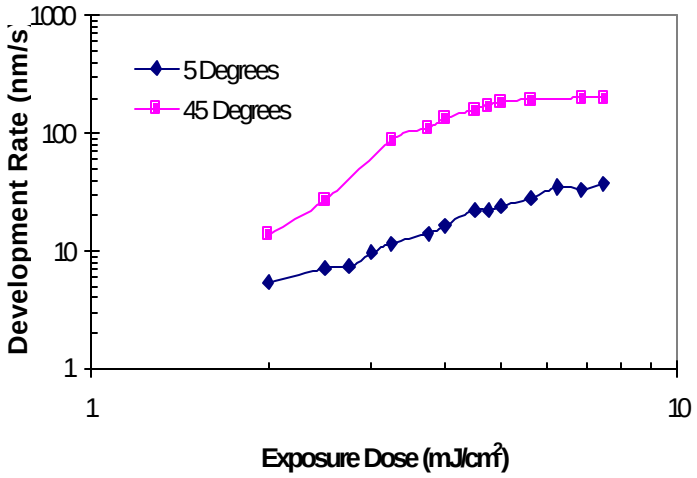


Figure 3: Development rate of APEX-E (averaged through the middle 20% of the resist thickness) as a function of exposure dose for different developer temperatures. At higher doses, higher developer temperature increases the dissolution rate. Higher developer temperature also increases the dissolution selectivity parameter *n*.

Figure 5 shows the final results of the analysis. All four parameters of the original Mack model of dissolution are plotted versus developer temperature in an Arrhenius plot. Dissolution parameters R_{min} and n go through behavior that cannot be accurately explained with Arrhenius plots at high developer temperature. Dissolution parameter R_{max} is described using two different Arrhenius fits. The break point occurs between developer temperatures of 30º and 35ºC. Table II shows the activation energies and Arrhenius coefficients resulting from the fit of this data.

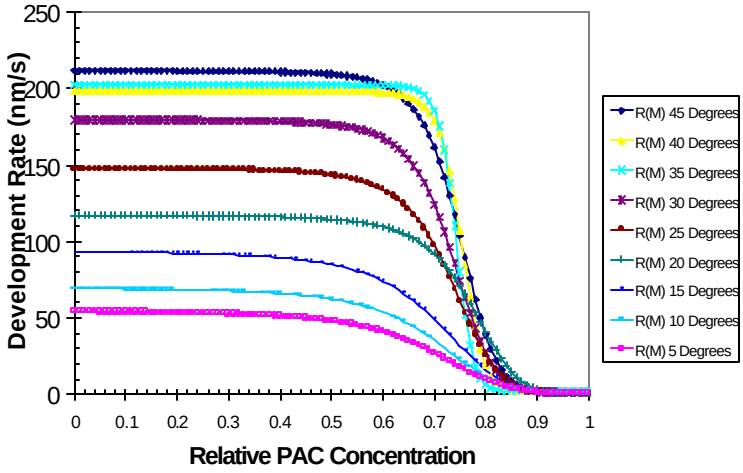


Figure 4: Comparison of the best-fit models of APEX-E for different developer temperatures shows the leveling off of develop rate at higher temperatures and exposure energies, the shift in m_{TH} and increasing dissolution selectivity parameter *n*.

Table II. Results of the fit of all dissolution parameters to an Arrhenius Relationship.

Develop Parameter	Activation Energy (Kcal/mol)	Arrhenius Coefficient	ln(Ar)
R_{max} [a]	8.2 / 0.9324	1.49×10^{8} / 903.22	18.42 / 6.81
R_{min} [b]	2.1779	61.257	4.12
m_{TH} [b]	0.0467	0.5673	-0.57
n [b]	3.2174	1262.5	7.14

Notes: a) R_{max} values for the two fits of the separate regions. Region 1: 5ºC - 30ºC Region 2: 35ºC - 45ºC
b) Results of fit using a temperature range of 5ºC - 30ºC

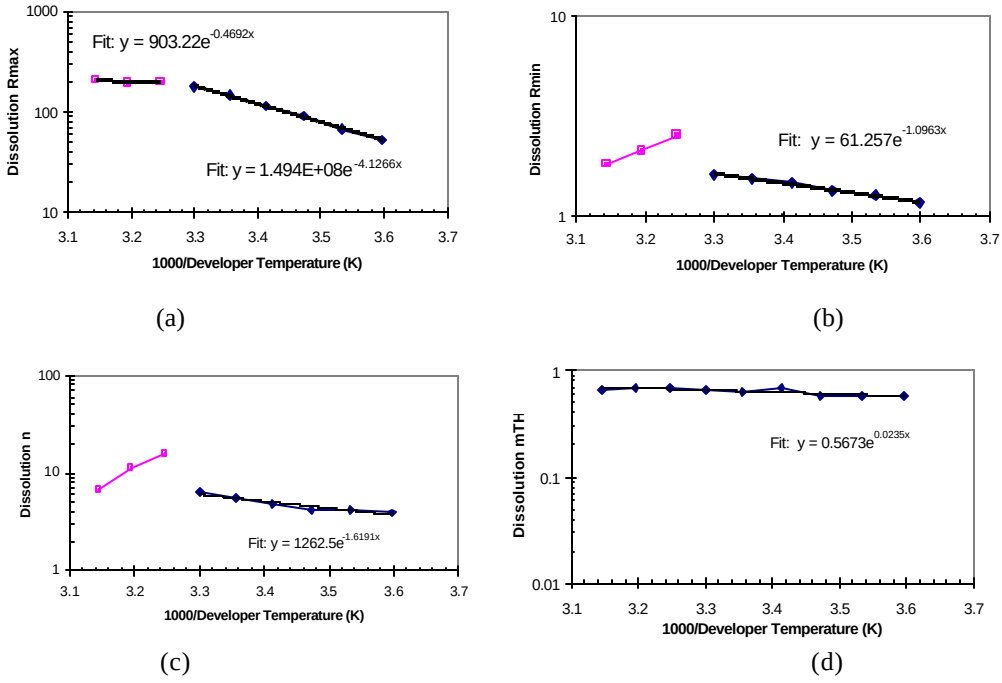


Figure 5. Arrhenius plots of (a) the maximum dissolution rate R_{max}, (b) the minimum dissolution rate R_{min}, (c) the dissolution selectivity parameter n, and (d) the threshold PAC concentration m_{TH}. Best fits to the Arrhenius equation are also shown.

Table III. Developer Temperature Dependent Modeling Parameters of APEX-E (0.26N developer)

Developer Temperature	R_{max} (nm/s)	R_{min} (nm/s)	m_{TH}	n
5° C	53.14 ± 8.96	1.176	0.571 ± 0.036	3.931 ± 0.556
10° C	67.97 ± 10.87	1.2833	0.578 ± 0.031	4.169 ± 0.519
15° C	91.93 ± 13.81	1.349	0.586 ± 0.028	4.250 ± 0.485
20° C	115.66 ± 14.1	1.482	0.682 ± 0.016	4.786 ± 0.488
25° C	146.05 ± 15.21	1.554	0.637 ± 0.015	5.562 ± 0.544
30° C	177.83 ± 15.99	1.621	0.646 ± 0.012	6.355 ± 0.554
35° C	199.65 ± 14.56	2.562	0.693 ± 0.008	15.578 ± 2.171
40° C	196.17 ± 13.14	2.135	0.694 ± 0.008	11.247 ± 1.321
45° C	209.54 ± 22.52	1.834	0.665 ± 0.014	6.642 ± 0.736

4 - 2. Developer Normality Effects

The data for the study of the effect of developer normality was collected using Shipley CD-26 developer, diluted to 0.13, 0.195, 0.24425 and full strength (0.26) normalities at 20ºC, 35ºC, and 40ºC developer temperatures. The variation of the dissolution rate behavior with developer normality was similar to the variation with developer temperature. In general, one expects kinetic rate limited reactions to proceed slower at lower normalities. As can be seen in Figure 6, at a given depth into the resist (again, the middle 20% of the resist was used) the development rate is slowed for all exposure energies as the normality is decreased. Data collected at 0.13 N did not see sufficient dissolution to be included in the full analysis.

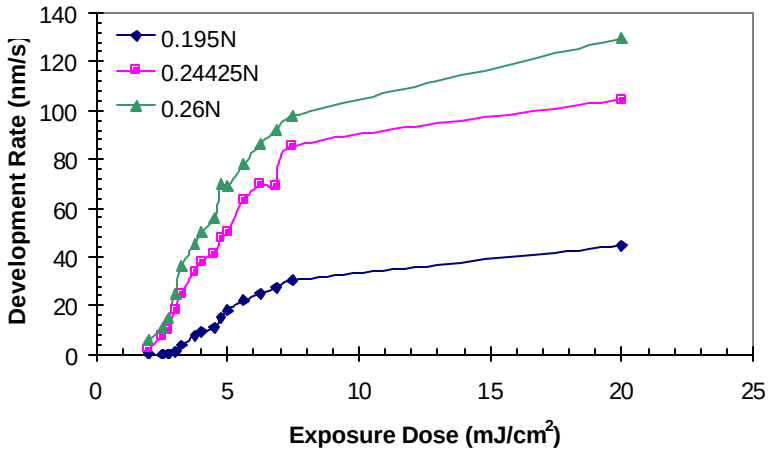


Figure 6: Development rate of APEX-E (averaged through the middle 20% of the resist thickness) as a function of exposure dose for different developer normalities at a developer temperature of 20ºC. At all doses, lower developer normality decreases the dissolution rate, with higher doses receiving the greatest decrease. Lower developer normality also decreases the dissolution selectivity parameter *n*.

In fitting the dissolution behavior to a development model, the variation of the *R(m)* curve with normality at a developer temperature of 35°C is shown in Figure 7. Again, the top and bottom 20% of the resist was excluded in order to eliminate surface and substrate effects. The analysis of the bulk development behavior shows that as normality decreases, the maximum development rate (R_{max}) decreases. At lower doses (higher concentrations of PAC) a shift in the threshold PAC concentration m_{TH}, and a decrease in the dissolution parameter *n* result in more complicated dissolution rate behavior. Measuring R_{min} without including surface effects requires considerable care and was not attempted. Simple R_{min} calculations were performed on unexposed sites measured before and after development.

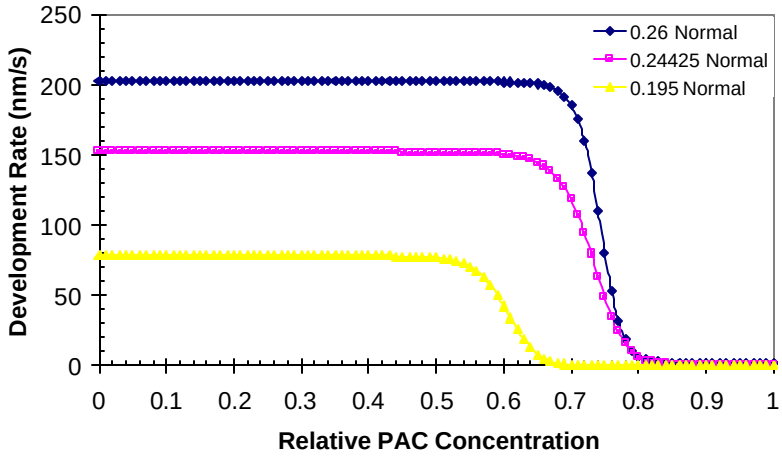
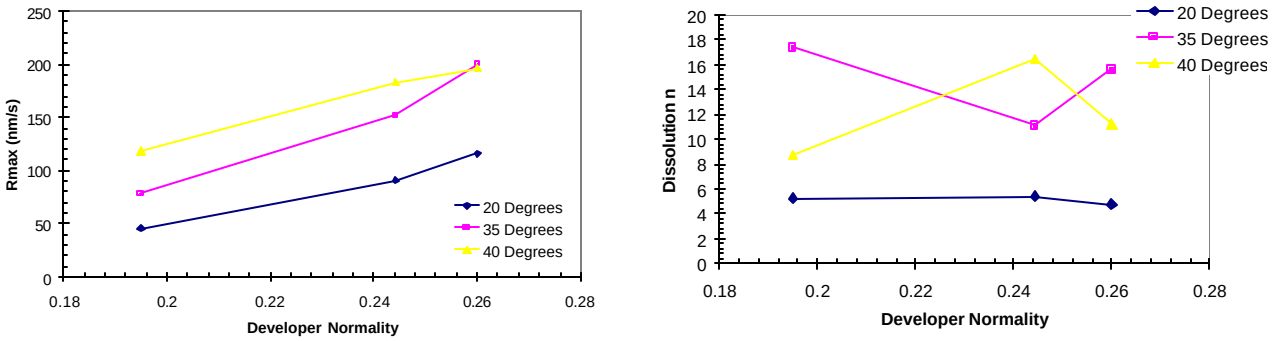


Figure 7: Comparison of the effect of developer normalities on the development rate of APEX-E at 35°C developer temperature. Shows the effects of decreasing maximum dissolution rate R_{ma}, and shift in m_{TH}

Figure 8 shows the final results of the analysis. The original Mack model parameters R_{max} and the dissolution selectivity parameter n are shown to vary with developer normality. As the developer temperature increases, the impact of different developer normalities on R_{max} is lessened. The impact of normality on the dissolution selectivity n is quite complicated.



(a) (b)

Figure 8: Plots of (a) the maximum dissolution rate R_{max}, and (b) the dissolution selectivity parameter n versus developer normality for different developer temperatures. At higher temperatures the effect of the developer normality is diminished on R_{max} and is erratic on the dissolution selectivity parameter n.

Table IV: Developer Normality Dependent Modeling Parameters

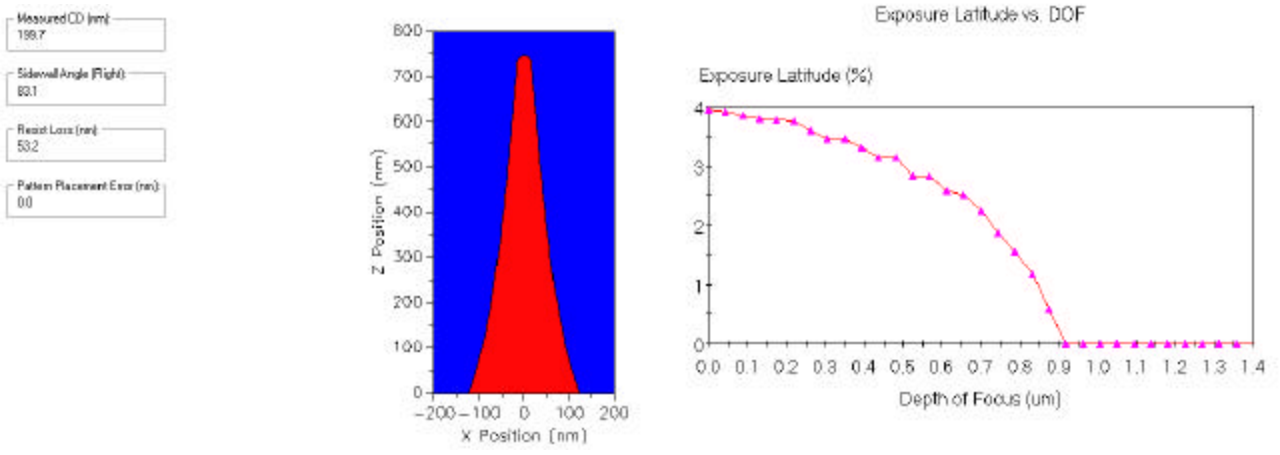
Developer Temperature	Developer Normality	R_{max} (nm/s)	R_{min} (nm/s)	m_{TH}	n
20°C	0.195	45.88 ± 7.93	0.272	0.527 ± 0.03	5.263 ± 1.002
20°C	0.24425	90.93 ± 11.27	0.9121	0.607 ± 0.018	5.408 ± 0.607
20°C	0.26	115.66 ± 14.1	1.482	0.682 ± 0.016	4.786 ± 0.488
35°C	0.195	78.08 ± 12.91	0.3953	0.533 ± 0.01	17.329 ± 2.176
35°C	0.24425	151.33 ± 13.07	1.191	0.667 ± 0.008	11.091 ± 1.14
35°C	0.26	199.65 ± 14.56	2.562	0.693 ± 0.008	15.578 ± 2.171
40°C	0.195	118.49 ± 94.6	0.3953	0.511 ± 0.074	8.715 ± 1.925
40°C	0.24425	182.86 ± 12.36	1.473	0.675 ± 0.005	16.441 ± 1.617
40°C	0.26	196.17 ± 13.14	2.135	0.694 ± 0.008	11.247 ± 1.321

5. SIMULATION RESULTS

The standard process flow for APEX-E at SEMATECH calls for Shipley MF-702 (0.21N) developer at room temperature (22°C) for 84 seconds. The modeling parameters measured for MF-702 at 20°C are shown in Table V. Using the parameters listed in Table I, simulations of a binary 200nm line/space pattern were performed using PROLITH/3D v6.0.4 [8]. The simulations included an optimized bottom ARC layer. At best focus, the standard process resist profile is shown in Figure 9. In comparison, the resist profile at best focus using the modeling parameters for a 35°C, 0.195N develop process is shown in Figure 10. The only changes made were the dose to size and the developer model.

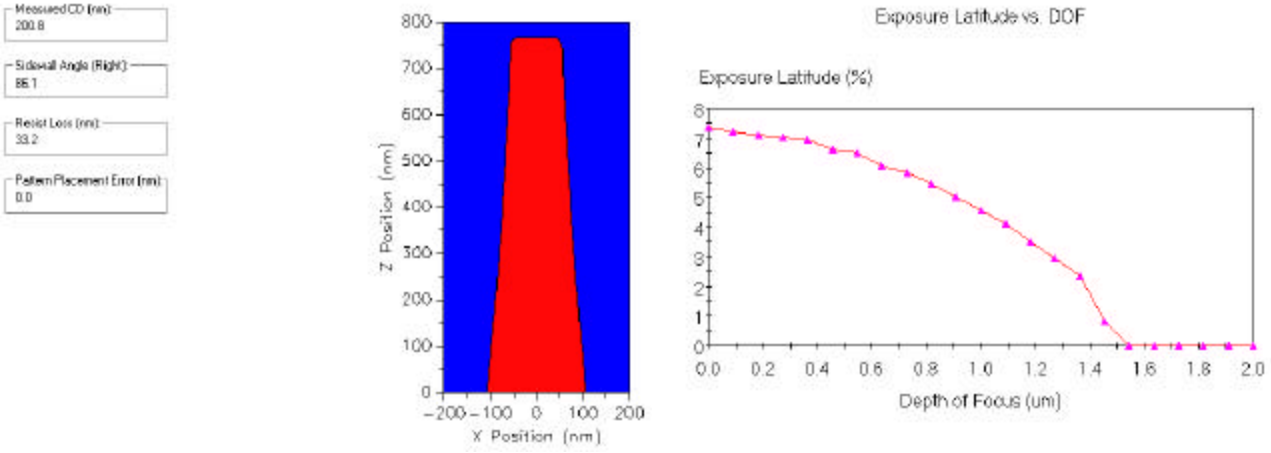
Table V. MF-702 (20°C) Developer Modeling Parameters

R_{max} (nm/s)	64.54 ± 9.48
R_{min} (nm/s)	0.397
m_{TH}	0.577 ± 0.022
n	5.293 ± 0.842



(a) (b)

Figure 9. PROLITH simulated (a) resist profile for a binary 200nm line/space feature using MF-702 Developer at 20°C, and (b) Exposure Latitude vs. DOF analysis of a Focus-Exposure Matrix.



(a) (b)

Figure 10. PROLITH simulated (a) resist profile for a binary 200nm line/space feature using CD-26 developer (diluted to 0.195N) at 35°C, and (b) Exposure Latitiude vs. DOF analysis of a Focus-Exposure Matrix

6. CONCLUSIONS

By parameterizing the effects of developer temperature and developer normality with the coefficients to a development model, one is able to characterize a complicated reaction in a relatively simple, straightforward manner. For the results studied here the Mack development model provided good fits to the experimental data over the full range of developer temperatures and normalities. All of the model parameters showed Arrhenius behavior with developer temperature to different degrees. R_{max} had two distinct Arrhenius regions, leading one to believe there is a significant change to the reaction at temperatures above 30ºC. The non-Arrhenius behavior of R_{min} and n above 30ºC also point to this conclusion. The normality study showed similar results where stronger normal developers had the higher R_{max} parameter. The combined effects of developer temperature and developer normality show that optimizations can be made to these settings to help improve the develop process. The simulation results for high-temperature low-normality systems show that process improvements can be made with modifications to the developer temperature and normality conditions.

Further work would include further normality experiments with smaller steps between different normality levels. Further study of other chemically amplified resists which are based on different resin structures is also needed. Finally, comparisons of simulated resist profiles using developer temperature and normality dependent parameters with experimentally collected samples must be performed.

7. REFERENCES

1. C. A. Mack, M. J. Maslow, A. Sekiguchi, R. Carpio, "New Model for the Effect of Developer Temperature on Photoresist Dissolution," *Advances in Resist Technology and Processing XV, Proc.*, SPIE Vol. 3333 (1998) pp. 169-142.
2. Litho Tech Japan Corporation, 2-6-6-201, Namiki, Kawaguchi, Saitama 332, Japan.
3. A. Sekiguchi, C. A. Mack, Y. Minami, T. Matsuzawa, "Resist Metrology for Lithography Simulation, Part 2: Development Parameter Measurements," *Metrology, Inspection, and Process Control for Microlithography X, Proc.*, SPIE Vol. 2725 (1996) pp. 49-63.
4. C. A. Mack, "Development of Positive Photoresist," *J. Electrochemical Society,* Vol. 134, No. 1 (Jan. 1987) pp. 148-152.

5. C. A. Mack, "New Kinetic Model for Resist Dissolution," *J. Electrochemical Society*, Vol. 139, No. 4 (Apr. 1992) pp. L35-L37.
6. C. A. Mack and G. Arthur, "Notch Model for Photoresist Dissolution," *Electrochemcial and Solid State Letters*, Vol. 1, No. 2, (August, 1998) pp. 86-87.
7. FINLE Technologies, Inc., P.O. Box 162712 Austin, TX 78716
8. C. A. Mack, Inside PROLITH: A Comprehensive Guide to Optical Lithography Simulation, FINLE Technologies (Austin, TX: 1997).