New Model for the Effect of Developer Temperature on Photoresist Dissolution

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ABSTRACT

The effects of developer temperature on dissolution behavior for eight g-line and i-line resists, ranging from first-generation to state-of-the-art formulations, are characterized using development rate measurements. Using the RDA-790 development rate measurement tool, dissolution rates as a function of dose and depth into the resist were measured. Each data set was analyzed and the basic performance of rate versus photoactive compound (PAC) concentration was fit to appropriate models. The variation of these results with temperature of the developer solution has led to temperature-dependent characterization of the dissolution modeling parameters. Two such parameters, the maximum dissolution rate R_{max} and the dissolution selectivity parameter n, are shown to exhibit an Arrhenius behavior with well defined activation energies.

Keywords: Photoresist Development, Developer Temperature, Lithography Simulation, PROLITH

INTRODUCTION

It is well known that the temperature of the developer solution during development can have a significant impact on resist performance. The speed (i.e., overall development rate) varies in a complicated way with temperature, usually resulting in the counter-intuitive result of a "faster" resist process (i.e., a process requiring lower exposure doses) at lower developer temperatures. The shape of the development rate versus dose (or versus sensitizer concentration) curve will also vary considerably with temperature, leading to possibly significant performance differences. Although some good work has been published in this area [1-4], insufficient effort has been made to systematically characterize the lithographic impact of developer temperature in a quantitative way.

This paper characterizes the effects of developer temperature on dissolution behavior for eight g-line and i-line Novolak/DNQ resists in tetra-methyl ammonium hydroxide (TMAH) developers using development rate measurements. Resists were chosen to encompass a wide range of performances, from first-generation to state-of-the-art photoresists. Using the RDA-790 development rate measurement tool, dissolution rate as a function of dose and depth into the

resist was measured. Each data set was analyzed with the ProDRM software package and the basic performance of rate versus photoactive compound (PAC) concentration fit to appropriate models. The variation of these results with temperature of the developer solution has led to temperature-dependent characterization of the dissolution modeling parameters.

Once a model has been established for the temperature dependence of the dissolution behavior, resist performance versus developer temperature can be simulated in a comprehensive manner that is not practical based solely on experimental data. The result can be a meaningful optimization of developer temperature, estimation of lithographic errors due to developer temperature variations, and a general method for characterizing developer temperature effects on dissolution behavior.

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 [5]:

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

where R_{max} is the maximum (fully exposed, $m=0$) dissolution rate, R_{min} is the minimum (unexposed, $m=1$) dissolution rate, n is the dissolution selectivity (which corresponds to the surface reaction order), and a is a simplifying constant given by

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

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 [6] and the "notch" model of Mack and Arthur [7]. 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).

$$R \; = \; R_{\max}(1-m)^n \left| \frac{(a+1)(1-m)^{n\_notch}}{a+(1-m)^{n\_notch}} \right| + R_{\min} \qquad (3)$$

where

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

The term in the brackets of equation (6) 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 (6) 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 before [1-4]. The results show a complicated behavior where changes in developer temperature give 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 [2,3]. Use of a dissolution rate model can simplify the description of temperature effects by showing just the change in the model parameters with developer temperature.

EXPERIMENTAL

One *g*-line and seven *i*-line photoresists were studied in order to understand the impact of developer temperature on dissolution rate behavior. The *g*-line resist OFPR-800 is one of the oldest photoresists still in use in the semiconductor industry and is known as a low contrast resist. THMR-iP3650 by TOK, SPR505 by Shipley, SPR510L, a dyed version of 505, and Clariant's AZ7518 are mid-contrast *i*-line resists in common use. TOK's TDMR-AR80, Shipley's SPR955, and JSR's PFR-iX1040G are state-of-the-art high contrast *i*-line resists. Each resist was coated on bare silicon wafers to thicknesses of about 0.6 – 1.8 µm. The softbake and post-exposure bake (PEB) conditions for each resist, as well as the specific developer used, are given in Table I. All developers are TMAH-based.

All resists were measured in the RDA-790 resist development analyzer made by Litho Tech Japan [8]. This tool uses a measurement head with 18 channels to provide reflectance interferometry on 18 exposure sites on a 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.

All resists were measured at developer temperatures from 14ºC to 30ºC in 2ºC increments, except SPR505, SPR955 and AZ7518 which used an extended range of 5ºC to 45ºC

in 5ºC increments. Example results for the THMR-iP3650 resist are shown in Figure 1. The data was then analyzed in the ProDRM software package to convert the rate versus dose and depth in the resist, $R(E,z)$, into rate versus PAC concentration, $R(m)$, and then fit to a development model. The original Mack model of equation (1) was found to give good fits to all data sets, with the exception of the notch behavior exhibited by the three high contrast resists as described below.

Table I. Processing conditions for each resist.

Resist	Softbake Temp. (ºC)	Softbake Time (sec)	PEB Temp. (ºC)	PEB Time (sec)	Developer
OFPR-800	90	60	none	none	NMD-W
THMR-iP3650	90	90	110	90	NMD-W
SPR505	95	60	115	60	MIF702
SPR510L	95	60	115	60	MIF702
AZ7518	95	60	115	60	NMD-W
SPR955	95	60	115	60	NMD-W
TDMR-AR80	90	90	110	90	NMD-W
PFR-iX1040G	90	120	110	90	NMD-W

RESULTS

The variation of the dissolution rate behavior with developer temperature was similar for all resists but of greater or lesser degree depending on the resist. The basic behavior is illustrated in Figure 2. At a given depth into the resist (in this case, the middle 20% of the resist was used), the development rate as a function of incident dose can be plotted in a characteristic Hurter-Driffield like curve [9]. In general, one usually expects simple kinetic rate limited reactions to proceed faster at higher temperatures (indicating a positive activation energy for the reaction). The behavior shown in Figure 2 is obviously more complicated than that. At high doses, increasing developer temperature does increase the development rate. But at low doses the opposite is true. Thus, developer temperature has a significant impact on the shape of the dissolution rate curve, that is, on the resist contrast. Previous authors have proposed reasons for this behavior [2,3]. Here, we will strive to accurately describe this behavior quantitatively.

By fitting the dissolution rate behavior to a development model, the variation of the $R(m)$ curve with temperature can be shown, as in Figure 3. For this fitting, the top portion of the resist was excluded in order to eliminate surface inhibition effects and analyze only the bulk development behavior. Again, the results show that at high doses (corresponding to low concentrations of photoactive compound remaining) higher developer temperature increases the development rate. But at low doses (high concentrations of photoactive compound remaining),

the opposite is true. Using the terminology of the Mack development model, increasing the developer temperature caused an increase in the maximum development rate R_{max} and an increase in the dissolution selectivity parameter n. The threshold PAC concentration m_{TH} was found to be negative for most of the resists studied (and in the 0.0 – 0.15 range for a few) and did not vary significantly with temperature. Measurement of R_{min} exclusive of the surface inhibition effect requires special care and was not attempted in this study. The data showed that R_{min} was quite small for all resists (except OFPR-800) over the full temperature range.

Figures 4-6 show the final results of the analysis. The two parameters R_{max} and n are plotted versus developer temperature for each resist in an Arrhenius plot. Several resists exhibited significant standing waves for the conditions used and as a result showed somewhat noisier data than others. The activation energies and Arrhenius coefficients resulting from the fits of this data are given in Table II for R_{max} and Table III for the dissolution selectivity parameter n.

Table II. Results of the fit of R_{max} to an Arrhenius relationship.

Resist	Activation Energy (Kcal/mol)	Arrhenius Coefficient (nm/s)	ln(Ar)
OFPR-800	5.32	7.084×10^5	13.47
THMR-iP3650	7.41	3.368×10^7	17.33
SPR510L	5.12	2.895×10^5	12.58
SPR505	2.33 (5.16[a])	2.084×10^3 (5.40×10^4)	7.64 (10.90[a])
AZ7518	6.14	5.198×10^6	15.46
SPR955	5.14	7.986×10^5	13.59
TDMR-AR80	8.75	3.384×10^8	19.64
PFR-iX1040G	8.43	1.796×10^8	19.01

Notes: a) results of Arrhenius fit if only the 10 – 30ºC temperature range is used.

The three high contrast resists, SPR955, TDMR-AR80, and PFR-iX1040G, each exhibited a dissolution notch over part or all of the temperature range studied. It appeared as if the strength of the notch varied with temperature. However, accurate characterization of the notch, which requires dissolution rate measurements concentrated at doses near the notch position, was not carried out.

Examination of the data in Figures 4-6 and in Tables II and III shows that different resist have very different sensitivities to developer temperature. All of the resists showed basic Arrhenius behavior over the temperatures ranges studied except SPR505, which seemed to saturate at temperatures above 30ºC. The activation energies for R_{max} for all resists were in the

range of 5.1 – 8.8 Kcal/mole (an activation energy of E_a = 8 Kcal/mole means that R_{max} will approximately double over the temperature range of 15 – 30ºC; an activation energy of 5 Kcal/mole will increase R_{max} by about 50% over the same range). The impact of developer temperature on the dissolution selectivity parameter n was much more varied. AZ7518 showed virtually no temperature dependence with respect to n (E_a = 0.767 Kcal/mole) while PFR-iX1040G showed a tripling of the value of n as the temperature varied from 15 to 30ºC (E_a = 12.65 Kcal/mole).

Table III. Results of the fit of n to an Arrhenius relationship.

Resist	Activation Energy (Kcal/mol)	Arrhenius Coefficient (nm/s)	ln(Ar)
OFPR-800	2.26	5.998×10^1	4.09
THMR-iP3650	7.02	7.65×10^5	13.55
SPR510L	4.57	6.092×10^3	8.71
SPR505	5.19	5.398×10^4	10.90
AZ7518	0.767	1.132×10^1	2.42
SPR955	3.57	1.304×10^3	7.17
TDMR-AR80	10.31	2.824×10^8	19.46
PFR-iX1040G	12.65	1.627×10^{10}	23.51

LITHOGRAPHIC SIMULATIONS

What is the lithographic impact of these changes in dissolution rate behavior? An advantage of describing the effects of developer temperature as a variation in modeling parameters is the ease with which simulation can be employed to explore their impact. For example, does a resist get "faster" or "slower" as developer temperature is increased? If the "speed" of a photoresist is judged by its dose-to-clear (E_o) or its dose-to-size (E_S), it is not clear at first glance how the changes in development rate response shown above will affect resist speed. Using the lithography simulator PROLITH/2 [10], dose-to-clear and dose-to-size were simulated for THMR-iP3650 as a function of developer temperature. Figure 7 confirms the well-known result that colder developer results in a faster resist. This seemingly counter-intuitive result is explained by the increasing value of the dissolution selectivity parameter n with developer temperature.

Besides affecting resist speed, the dissolution selectivity parameter n is critical to resist performance. Figure 8 shows how lower temperatures, and the resulting lower n values, produce worse resist sidewall angles (in this case, exposure dose was adjusted to be the dose-to-size at the

temperature given). Although not shown, the lower temperatures will also result in smaller focus-exposure process windows.

Another valuable use of modeling is investigating the sensitivity of these resists to developer temperature variations. Figure 9 shows how two different resists will behave in the presence of temperature errors by plotting the resulting change in resist linewidth.

CONCLUSIONS

The impact of developer temperature on dissolution rate behavior would seem quite complicated if temperature were treated along with exposure dose and depth into the resist as simply another independent variable. The approach used here is to parameterize the effect of developer temperature on the coefficients of a development model. If the shape of the development rate versus exposure (or PAC concentration) curve is adequately fit by a given model over the temperature range of interest, the variation of each parameter of the model with temperature can be determined. If the model is well behaved, i.e., the resulting parameters as a function of developer temperature are smoothly varying, this approach can be used to completely describe the developer temperature effects.

For the resists studied here the Mack development model provided adequate fits to experimental data over the full range of developer temperatures, exclusive of any notch effects. Further, the model parameters R_{max} and n were found to vary smoothly with temperature and were fit extremely well with a simple and intuitive Arrhenius equation. The wide range of resists used indicate that this behavior may be applicable to all Novolak/DNQ resists in TMAH developers.

Future work includes the study of developer temperature on the dissolution notch and comparison of simulated with experimental linewidth response as a function of developer temperature.

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Development Rate (nm/s)

(a)

- E = .00 mJ/cm2
- E = 25 mJ/cm2
- E = 34 mJ/cm2
- E = 43 mJ/cm2
- E = 52 mJ/cm2
- E = 61 mJ/cm2
- E = 70 mJ/cm2
- E = 79 mJ/cm2
- E = 88 mJ/cm2
- E = 97 mJ/cm2
- E = 106 mJ/cm2
- E = 115 mJ/cm2
- E = 124 mJ/cm2
- E = 133 mJ/cm2
- E = 142 mJ/cm2
- E = 151 mJ/cm2
- E = 160 mJ/cm2
- E = 169 mJ/cm2
- E = 178 mJ/cm2
- E = 238 mJ/cm2
- E = 298 mJ/cm2
- E = 358 mJ/cm2
- E = 418 mJ/cm2

Depth into Resist (nm)

Development Rate (nm/s)

(b)

Depth into Resist (nm)
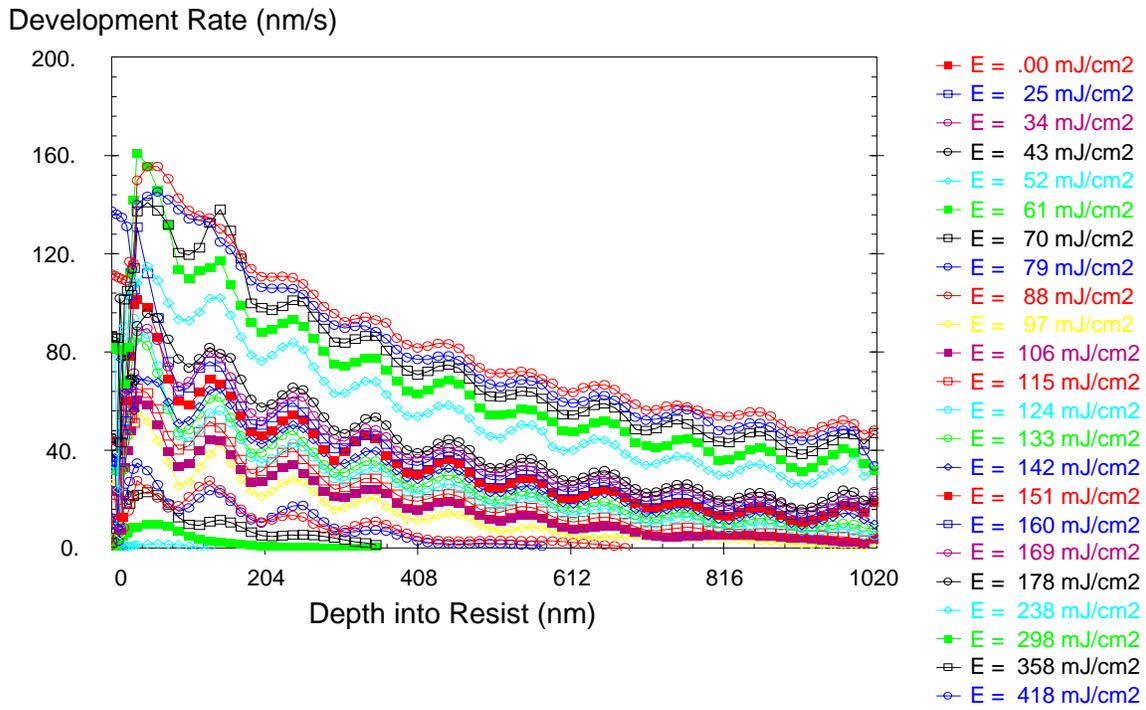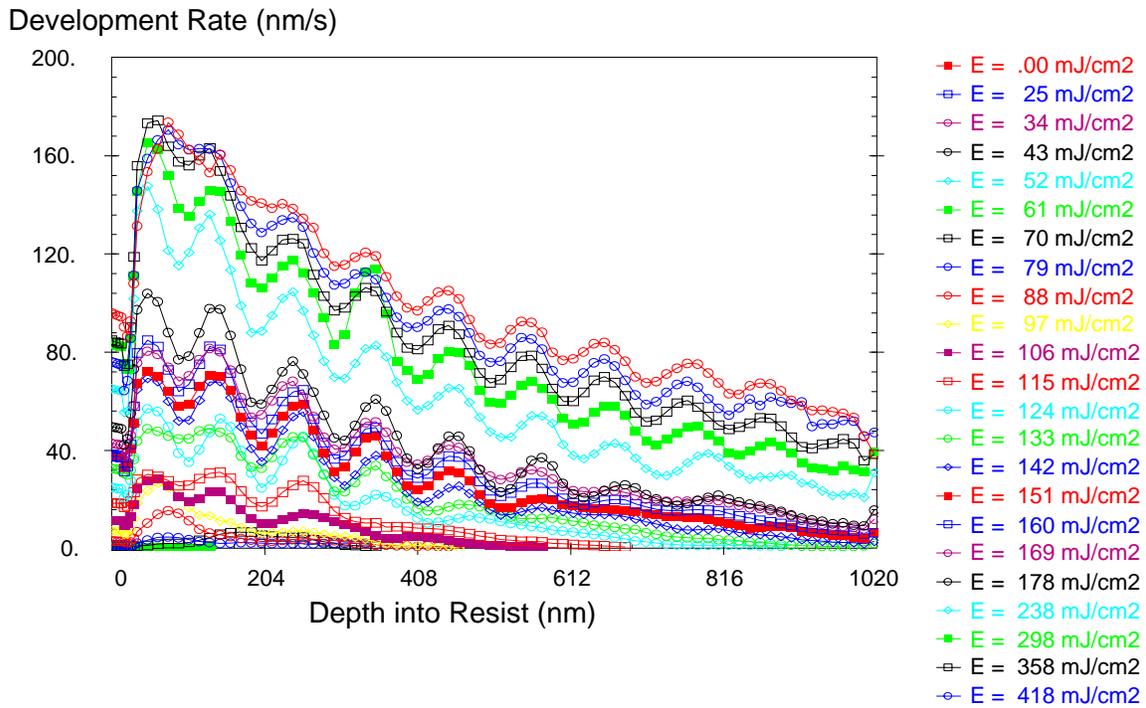
Figure 1. Dissolution rate data from the RDA-790 for THMR-iP3650 at developer temperatures of (a) 14°C and (b) 30°C.

Development Rate (nm/s)

Exposure Dose (mJ/cm²)
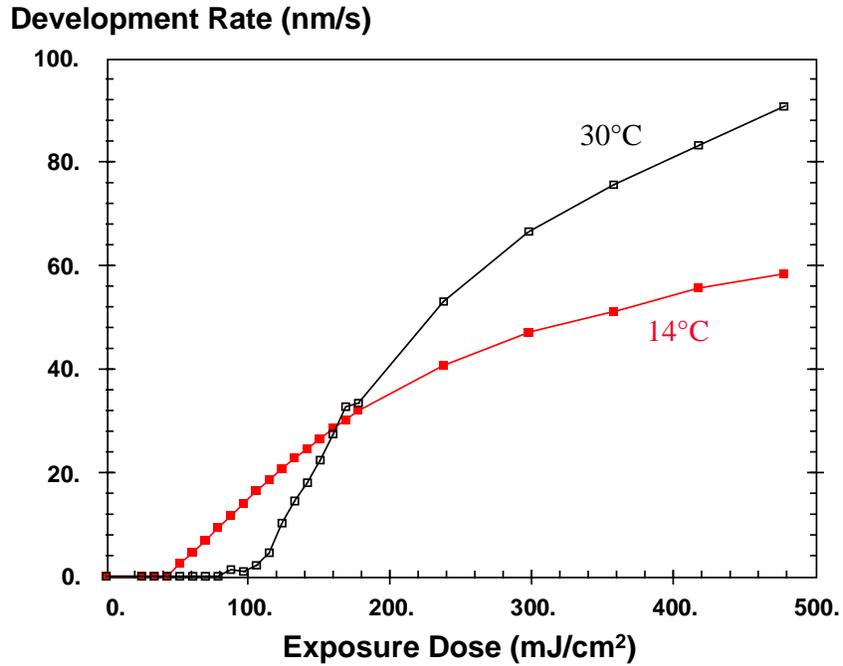
Figure 2.   Development rate of THMR-iP3650 (averaged through the middle 20% of the resist thickness) as a function of exposure dose for different developer temperatures shows a change in the shape of the development dose response. At higher doses, higher developer temperature increases the dissolution rate, whereas at lower doses the opposite trend occurs.

Development Rate (nm/s)

Relative PAC Concentration m
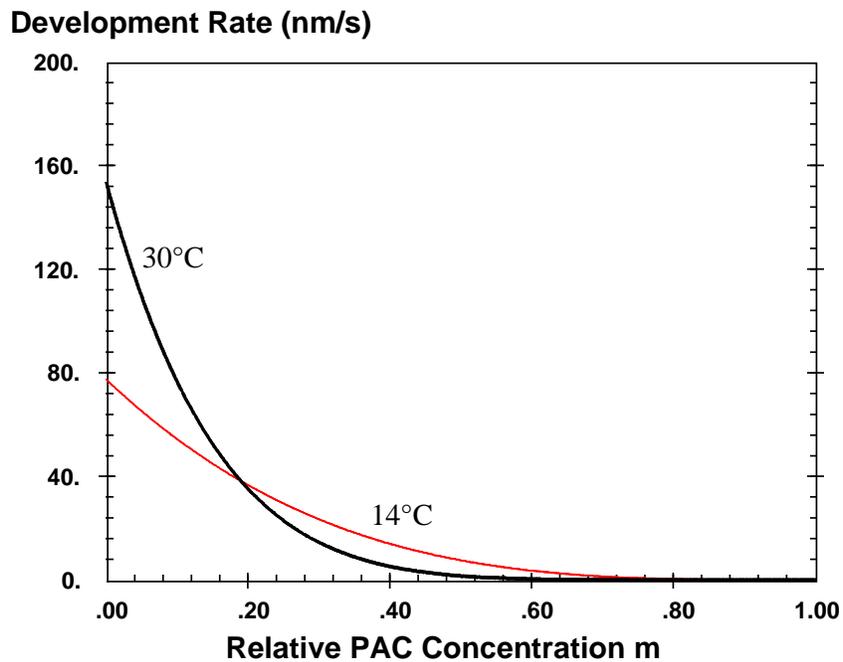
Figure 3.   Comparison of the best-fit models of THMR-iP3650 for different developer temperatures shows the effect of increasing R_{max} and increasing dissolution selectivity parameter n on the shape of the development rate curve.
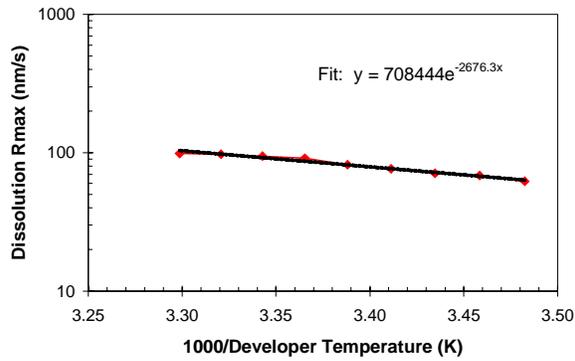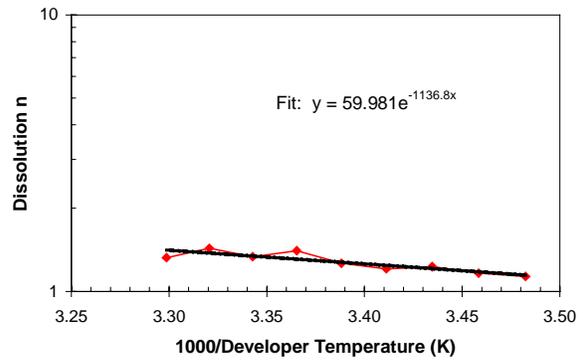
OFPR-800:   (a)   (b)
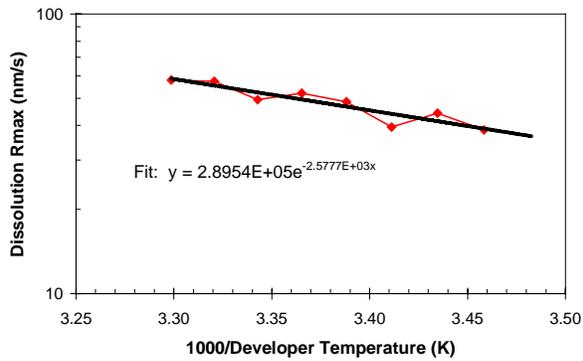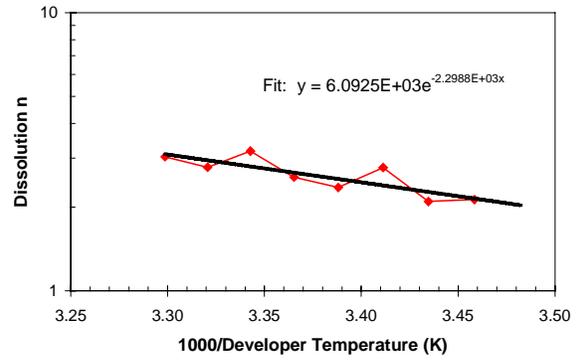

SPR510L: (c)   (d)
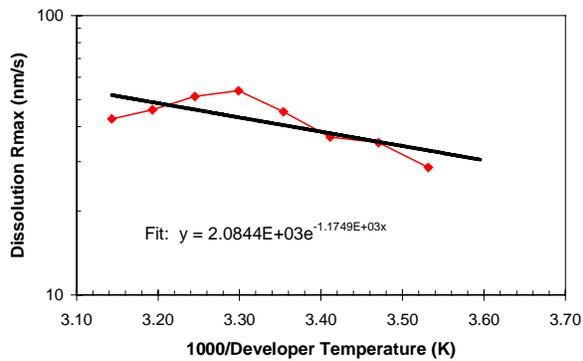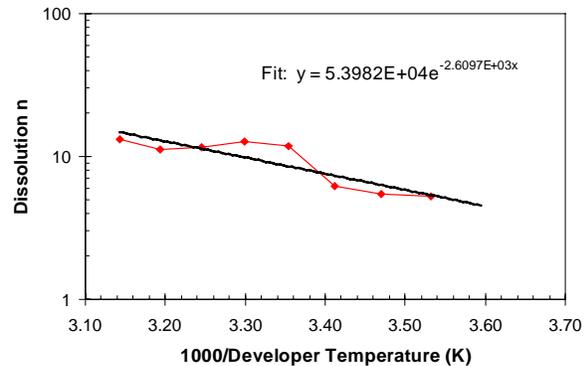
SPR505:   (e)   (f)

Figure 4.   Arrhenius plots of the maximum dissolution rate R_{max} and the dissolution selectivity parameter *n* for several photoresists. Best fits to the Arrhenius equation are also shown.

(a) Dissolution Rmax (nm/s) vs 1000/Developer Temperature (K)

Fit: $y = 3.3689E{+}07e^{-3.7282E{+}03x}$

(b) Dissolution n vs 1000/Developer Temperature (K)

Fit: $y = 7.6455E{+}05e^{-3.5309E{+}03x}$

THMR-iP3650:   (a)   (b)

(c) Dissolution Rmax (nm/s) vs 1000/Developer Temperature (K)

Fit: $y = 5.1975E{+}06e^{-3.0898E{+}03x}$

(d) Dissolution n vs 1000/Developer Temperature (K)

Fit: $y = 1.1324E{+}01e^{-3.8607E{+}02x}$

AZ7518:   (c)   (d)

(e) Dissolution Rmax (nm/s) vs 1000/Developer Temperature (K)

Fit: $y = 7.9855E{+}05e^{-2.5873E{+}03x}$

(f) Dissolution n vs 1000/Developer Temperature (K)

Fit: $y = 1.3043E{+}03e^{-1.7949E{+}03x}$
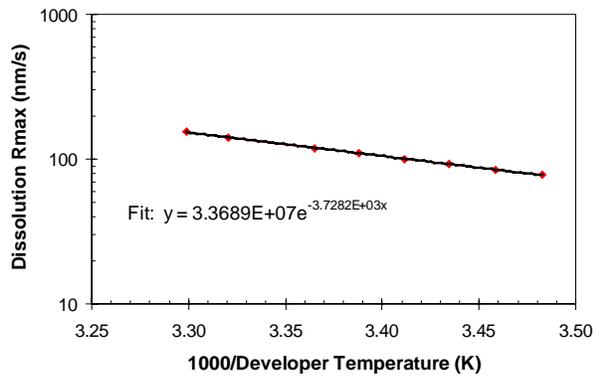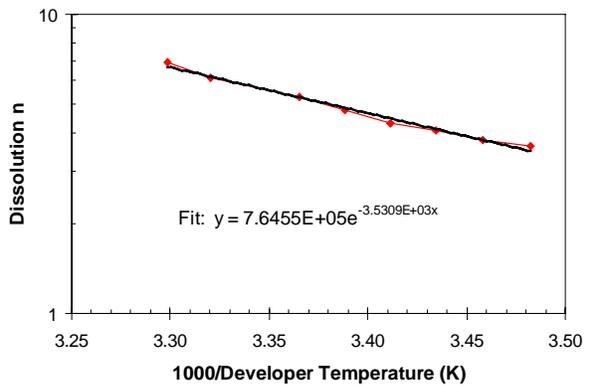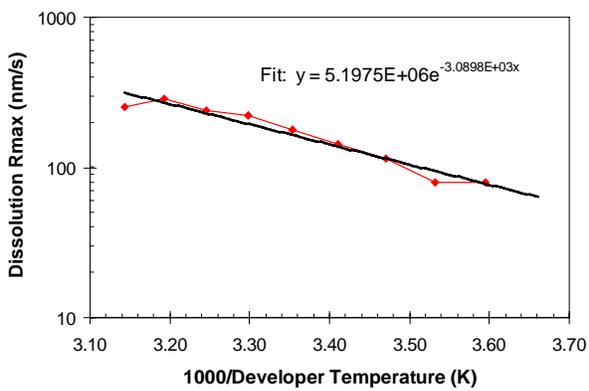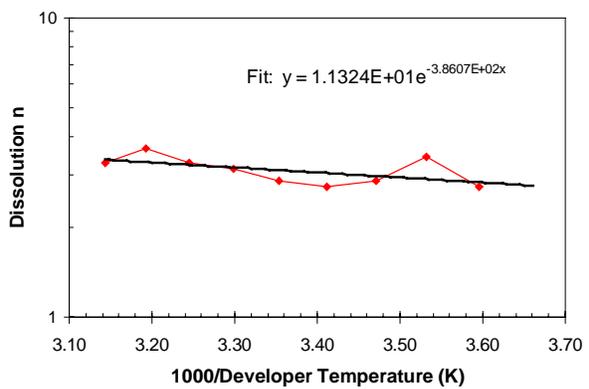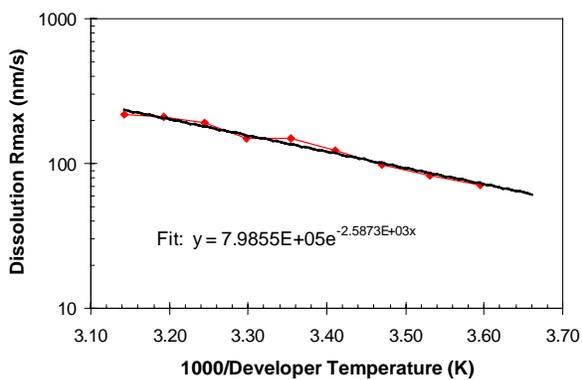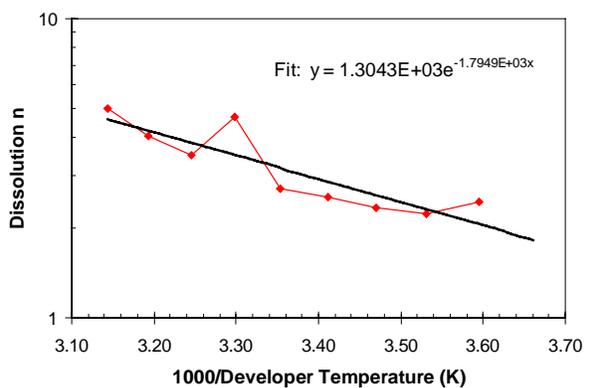
SPR955:   (e)   (f)

Figure 5. Arrhenius plots of the maximum dissolution rate R_{max} and the dissolution selectivity parameter n for several photoresists. Best fits to the Arrhenius equation are also shown.

Fit: y = 3.3840E+08e$^{-4.4057E+03x}$

Dissolution Rmax (nm/s)

1000/Developer Temperature (K)

TDMR-AR80: (a)

Fit: y = 2.8235E+08e$^{-5.1877E+03x}$

Dissolution n

1000/Developer Temperature (K)

(b)

Fit: y = 1.7956E+08e$^{-4.2401E+03x}$

Dissolution Rmax (nm/s)

1000/Developer Temperature (K)

PFR-iX1040G: (c)

Fit: y = 1.6273E+10e$^{-6.3683E+03x}$

Dissolution n

1000/Developer Temperature (K)
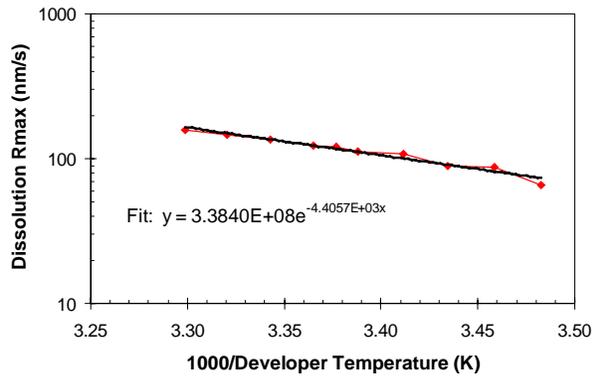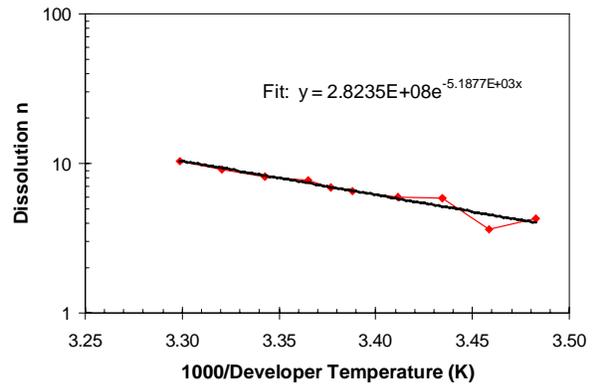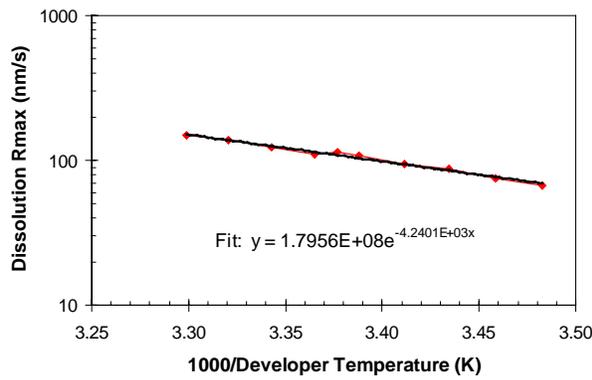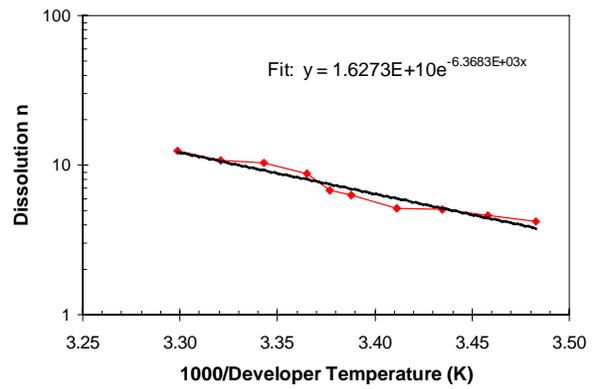
(d)

Figure 6.   Arrhenius plots of the maximum dissolution rate R_{max} and the dissolution selectivity parameter n for several photoresists. Best fits to the Arrhenius equation are also shown.
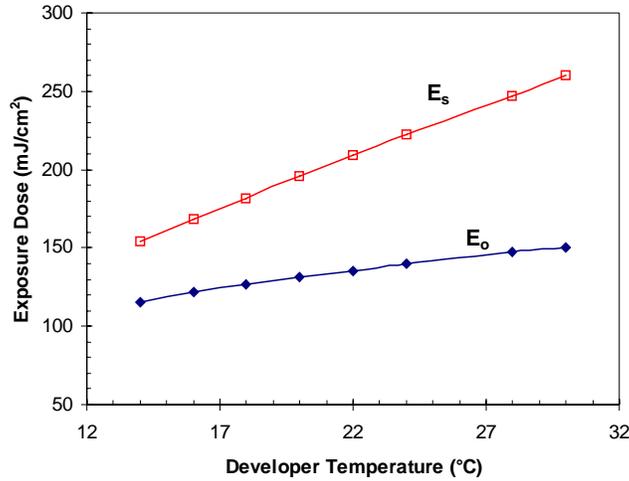
Figure 7. Simulated results of dose-to-clear (E_o) and dose-to-size (E_s) as a function of developer temperature for THMR-iP3650.


(a) (b) (c)
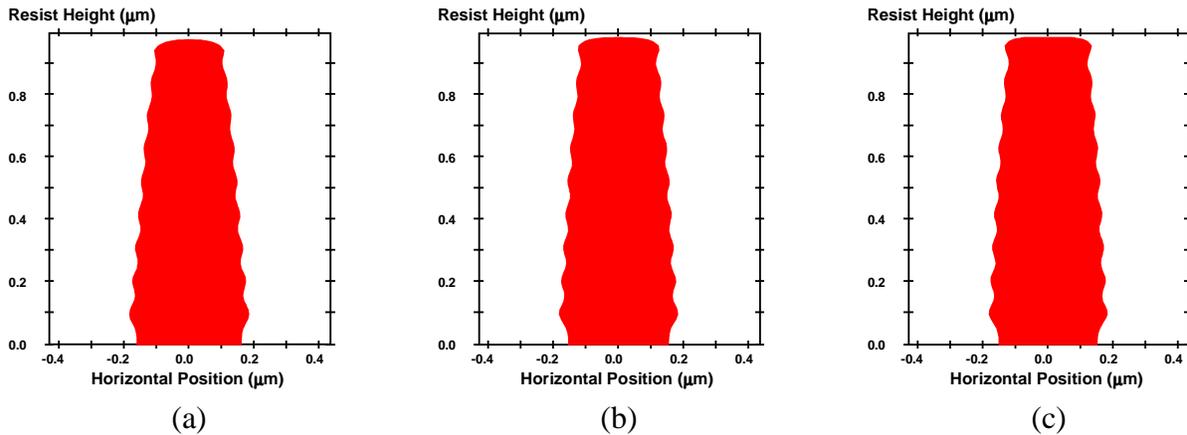
Figure 8. PROLITH/2 simulations showing the predicted effect of developer temperature on 0.35µm lines (NA = 0.6, σ = 0.5) for developer temperatures of (a) 14°C, (b) 22°C, and (c) 30°C for THMR-iP3650. Each profile is at the dose to size for that temperature.
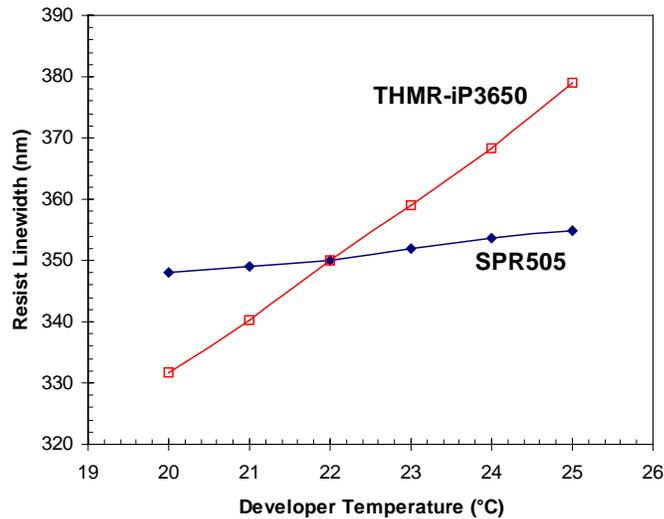

Figure 9. Simulated results of resist linewidth as a function of developer temperature for two resists.