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Impact of Developer Temperature on Dissolution Behavior

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ABSTRACT

The effects of developer temperature on dissolution behavior for two *i*-line resists are characterized using development rate measurements. Using the RDA-790 development rate monitor, dissolution rate 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 were 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.

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 at lower 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 [1-3], insufficient effort has been made to systematically characterize the lithographic impact of developer temperature.

This paper characterizes the effects of developer temperature on dissolution behavior for two *i*-line resists using development rate measurements. Using the RDA-790 development rate monitor, dissolution rate as a function of dose and depth into the resist was measured. Each data set was analyzed 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 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 [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

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

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

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

The effect of temperature on dissolution rate has been studied before [1-3]. 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 a different 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

Two *i*-line photoresists were studied in order to understand the impact of developer temperature on dissolution rate behavior. THMR-iP3650 by TOK and SPR510L, a dyed resist by Shipley, were coated on bare silicon wafers to thicknesses of about 1µm. The THMR-iP3650 wafers were softbaked at 90°C for 90 seconds and post-exposure baked at 110°C for 90 seconds. The SPR510L wafers were softbaked at 95°C for 60 seconds and post-exposure baked at 115°C for 60 seconds.

Both resists were measured in the RDA-790 development rate monitor made by Litho Tech Japan [5]. 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 0.02°C control of the developer temperature for immersion-mode (agitated with a magnetic stirrer) dissolution rate measurements.

Both resists were measured at developer temperatures from 14°C to 30°C in 2°C 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.

RESULTS

The variation of the dissolution rate behavior with developer temperature was similar for both resists but was more pronounced for the THMR-iP3650. 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 [6]. 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.

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 the fitting, the top 10% of the resist thickness 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 both resists studied and did not vary 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 both resists over the full temperature range.

Figures 4 and 5 show the final results of the analysis. The two parameters R_{max} and n are plotted versus developer temperature for both resists. The SPR510L resist seemed to exhibit significant standing waves for this process and as a result showed somewhat noisier data than the THMR-iP3650. In an attempt to describe the variation of these parameters with temperature

more thoroughly, each trend was fit with somewhat arbitrary functions. R_{max}, being indicative of a kinetic rate, was fit with an Arrhenius equation with excellent results. The activation energies and Arrhenius coefficients are given in Table I. The dissolution selectivity parameter n, indicative of a coordination number or reaction order for the development mechanism, was simply fit by a linear equation for lack of a better relationship.

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

Resist	Activation Energy (Kcal/mol)	Arrhenius Coefficient (nm/s)	ln(Ar)
THMR-iP3650	7.41	3.37×10^7	17.33
SPR510L	5.12	2.90×10^5	12.58

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 [7], dose-to-clear and dose-to-size were simulated for THMR-iP3650 as a function of developer temperature. Figure 6 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 7 shows how lower temperatures, and the resulting lower n values, produce worse resist sidewall angles. Although not shown, the lower temperatures will also result in smaller focus-exposure process windows.

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 two resists studied here the Mack development model provided adequate fits to experimental data over the full range of developer temperatures. Further, the model parameters R_{max} and n were found to vary smoothly with temperature. R_{max} was fit extremely well with a simple and intuitive Arrhenius equation. Resulting activation energies for THMR-iP3650 and SPR510L were 7.41 and 5.12 Kcal/mol, respectively. Of course, with a limited sample of only two resists it is not at all clear that all, or even most, resists will behave so regularly.

The work presented here provides an initial look at the impact of developer temperature on resist performance and presents a method for studying developer temperature effects using modeling parameters. Future work should include investigating more resists and looking over a wider temperature range.

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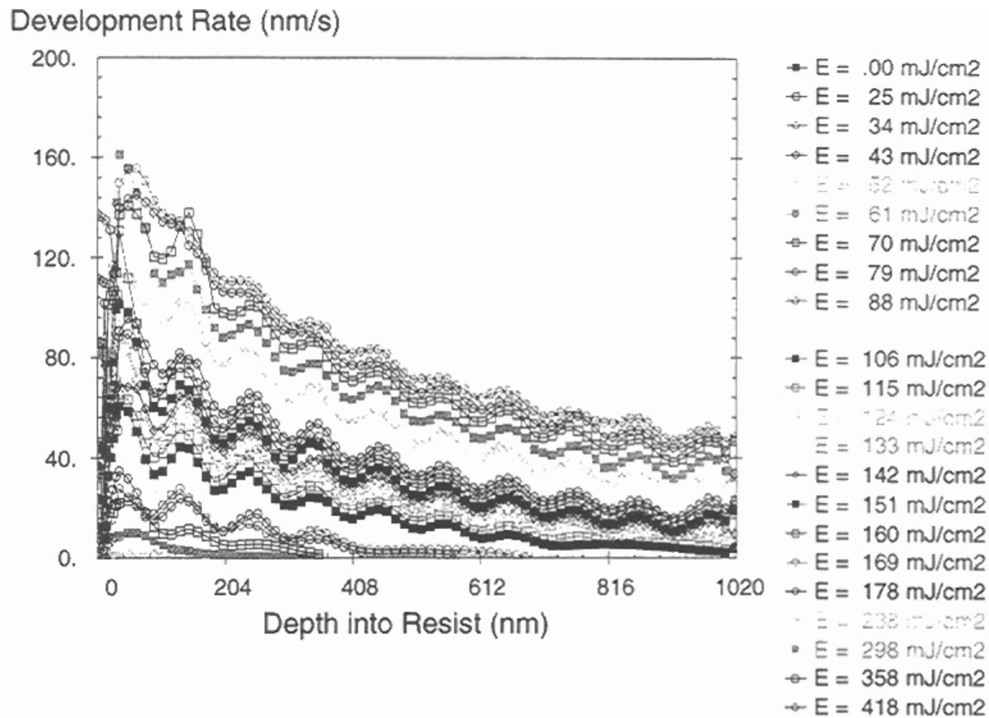
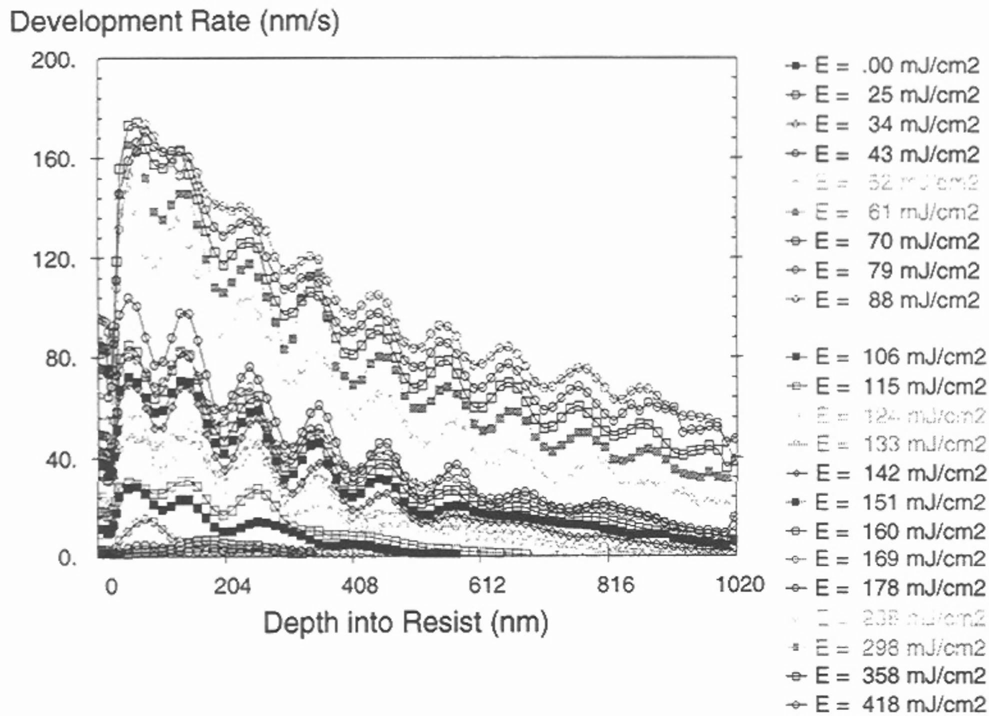


(a)



(b)

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

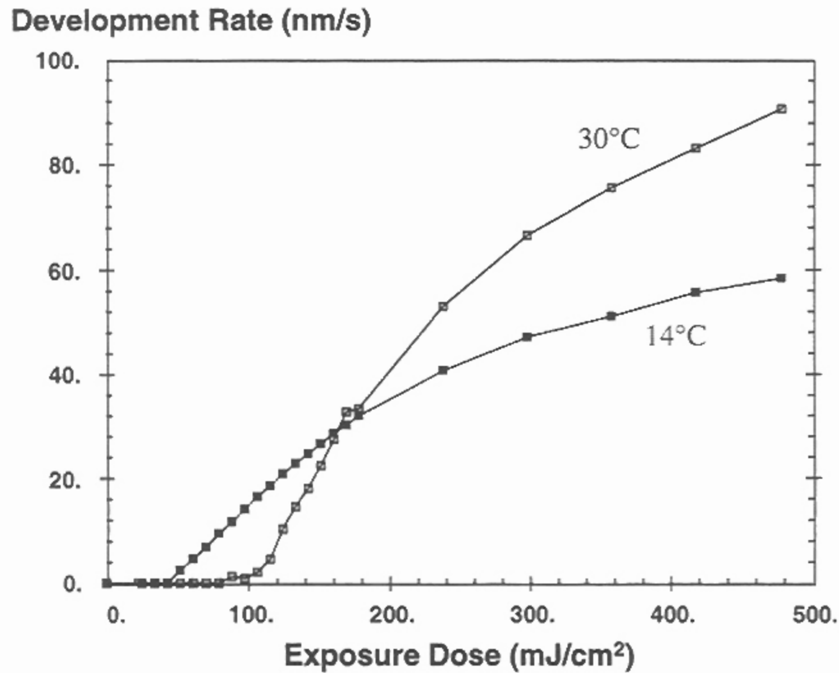


Figure 2. Development rate of THMR-iP3650 (averaged through the middle 20% of the resist thickness) as a function of exposure dose for different developer temperatures shows a change in the shape of the development dose response. At higher doses, higher developer temperature increases the dissolution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

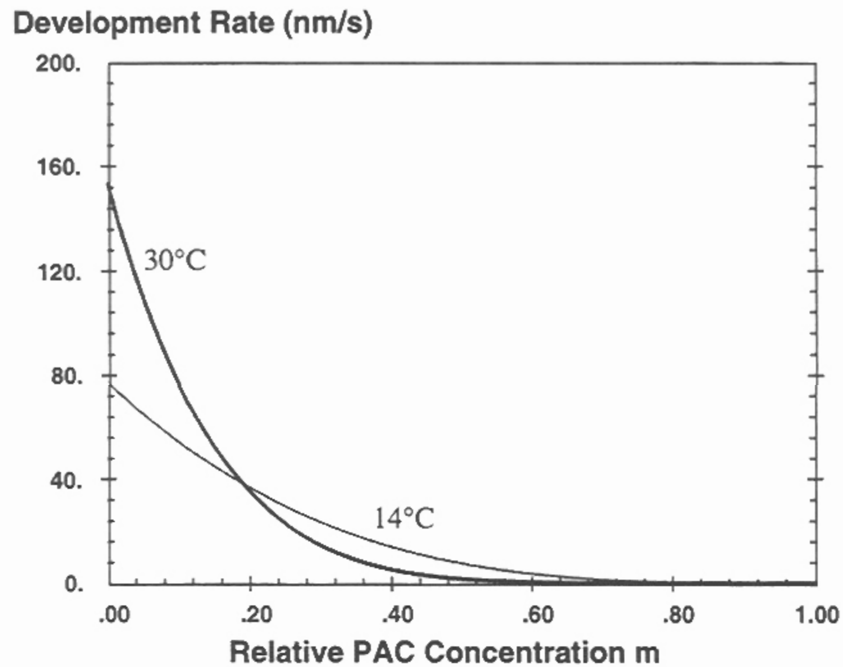


Figure 3. Comparison of the best-fit models of THMR-iP3650 for different developer temperatures shows the effect of increasing R_{max} and increasing dissolution selectivity parameter n on the shape of the development rate curve.

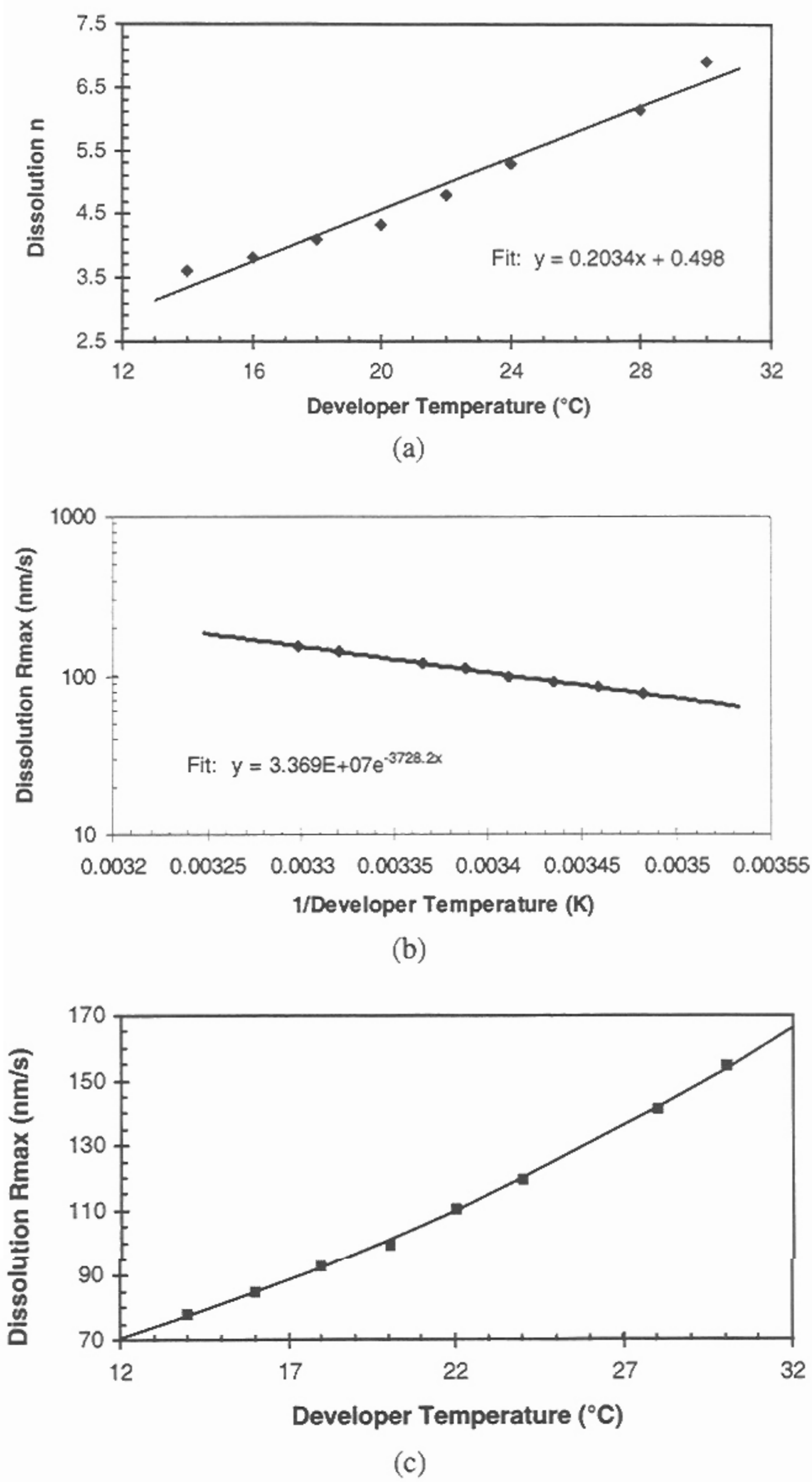
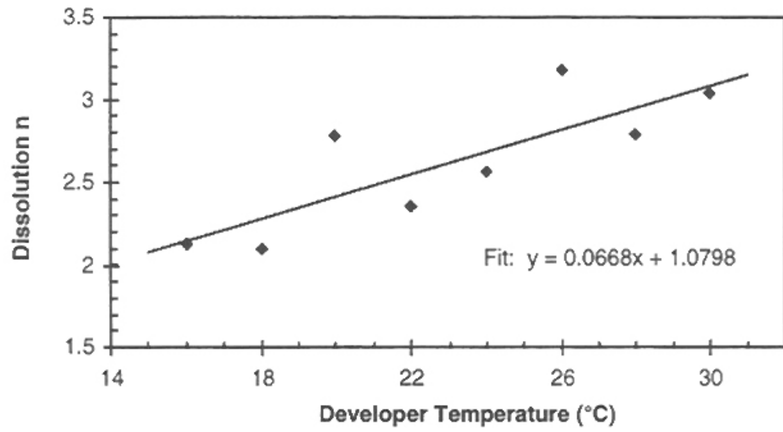
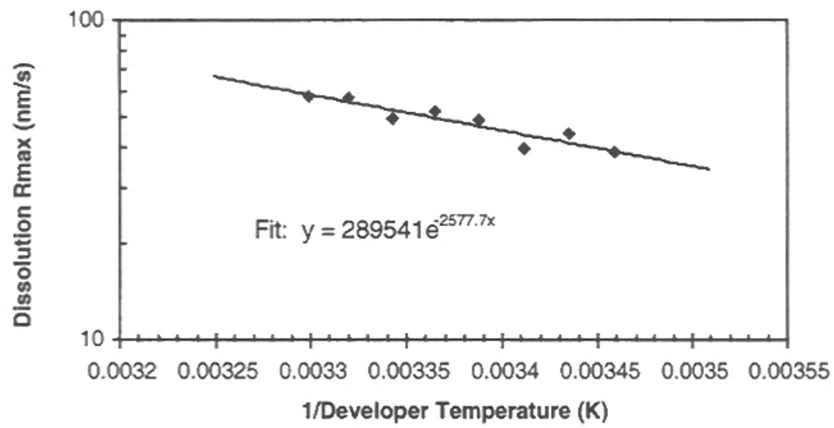


Figure 4. Trends of the dissolution selectivity parameter n and dissolution R_{max} as a function of developer temperature for THMR-iP3650.



(a)



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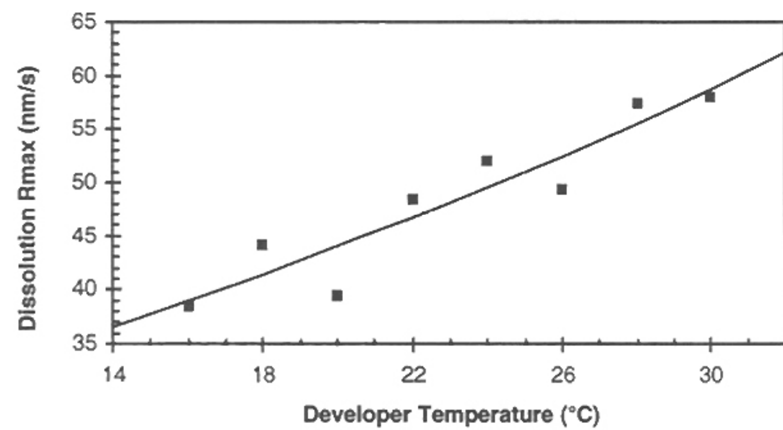

(c)

Figure 5. Trends of the dissolution selectivity parameter *n* and dissolution R_{max} as a function of developer temperature for SPR510L.

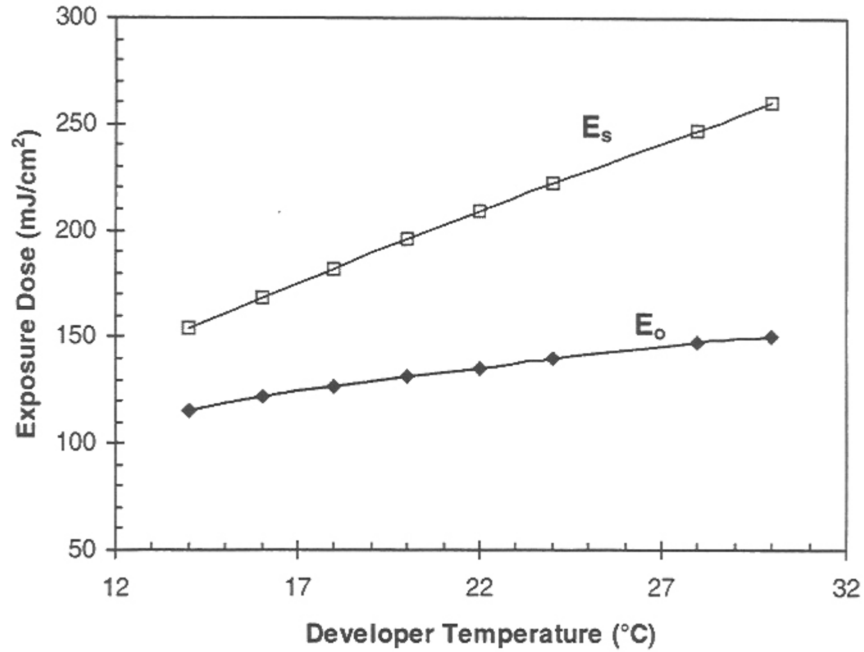

Figure 6. Simulated results of dose-to-clear (E_o) and dose-to-size (E_s) as a function of developer temperature for THMR-iP3650.

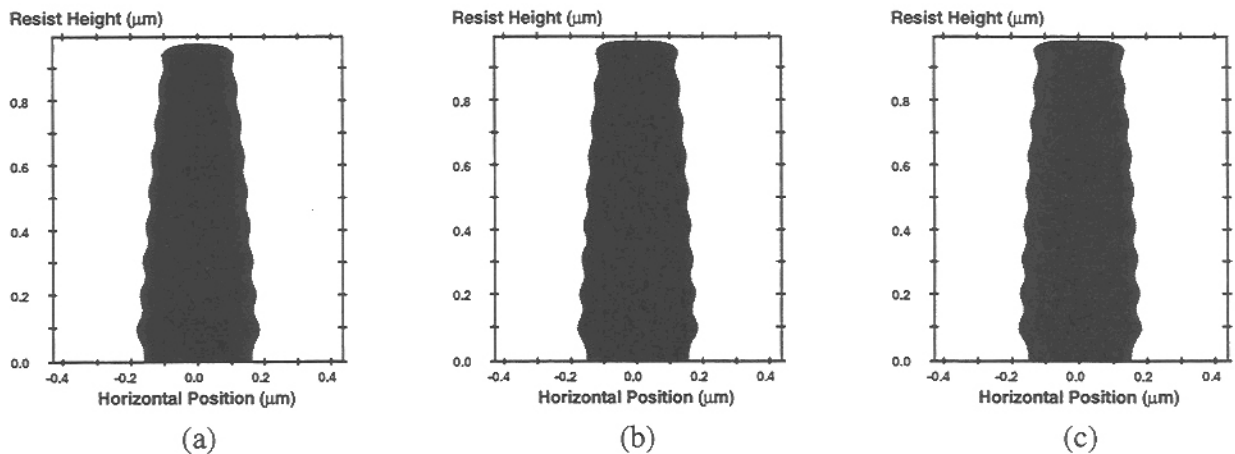

Figure 7. PROLITH/2 simulations showing the predicted effect of developer temperature on 0.35μm lines (NA = 0.6, σ = 0.5) for developer temperatures of (a) 14°C, (b) 22°C, and (c) 30°C for THMR-iP3650.