

# AN INTEGRATED APPROACH TO POSITIVE RESIST DEVELOPMENT CHARACTERIZATION

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## ABSTRACT

This paper investigates Neureuther and co-workers development model of positive novolak-type photoresist systems in aqueous alkaline developers. A measurement system for determining the exposure and development model parameters is described. The dissolution rates for two developer solutions have been examined and the impact of the developer differences on resist profiles is illustrated. The dissolution rate of resist in metal ion free developer at various temperatures is investigated.

## INTRODUCTION

Simulation is a well-established and essential tool in the design of integrated circuits. In the case of photolithography, accurate models and sets of parameters are required for various resists, developers, and processing conditions. Dill, et al. proposed the first models for exposure and development of positive photoresist [1].

The state of positive photoresist during exposure is described in terms of the normalized concentration of the inhibitor  $M(x,t)$ , which is the fraction of inhibitor remaining (at any depth in resist,  $x$ , and exposure time,  $t$ ) as compared to the inhibitor concentration before exposure. The function  $M(x,t)$  depends on the optical resist parameters  $A$ , difference in absorption between bleached and unbleached resist;  $B$ , absorption of fully bleached resist; and  $C$ , the rate of change of the resist absorption. Since there is little scattering in most photoresist film, the absorption constant,  $\alpha$ , can be expressed using Lambert-Beer Law.

$$\alpha = AM(x,t) + B \quad (1)$$

The total absorption of the photoresist film reduces as exposure converts the inhibitor to reaction products. For a positive photoresist:

$$dI(x,t)/dx = -I(x,t)[\alpha] \quad (2)$$

where  $I(x,t)$  is light intensity at any depth ( $x$ ) and time ( $t$ ) in the resist.



The rate of destruction of the inhibitor is dependent on the local optical intensity  $I(x,t)$ , the local inhibitor concentration, and  $C$ , as given by:

$$dM/dt = -I(x,t)M(x,t)C \quad (3)$$

Equations 2, and 3 are subject to the following initial conditions:

$$\begin{aligned} M(x,0) &= 1 \\ I(x,0) &= I_0 \exp[-(A+B)x] \end{aligned}$$

and boundary conditions:

$$\begin{aligned} I(0,t) &= I_0 \text{ (constant lamp intensity)} \\ M(0,t) &= \exp(-I_0 C t) \end{aligned}$$

One should note that equations 2 and 3 are coupled differential equations, and in order to determine  $I(x,t)$  and  $M(x,t)$ , these equations must be solved by numerical integration techniques, once the values for  $A, B, C$ , and  $I_0$  are known.

The values of  $A, B$ , and  $C$  are dependent on exposure wavelength. Techniques for measurement of these parameters have been described in detail by several authors [1-2]. The internal transmittance,  $T$ , of a photoresist film on a matched substrate is expressed as:

$$T(t) = \exp[-\int_0^d \{\alpha\} dx] \quad (4)$$

where  $d$  is the thickness of the resist film. Equation 4 may be used to derive relationships between the optical resist parameters and the optical transmittance of a resist film. These relationships are:

$$A = (1/d) \ln[T(\infty)/T(0)] \quad (4a)$$

$$B = -(1/d) \ln T(\infty) \quad (4b)$$

$$C = [(A+B)/A][1/T(0)][1/1-T(0)][dT(0)/dt] \quad (4c)$$

Figure 1 represents a typical apparatus for measuring transmittance of a resist film. A glass substrate with the same index of refraction as the photoresist is utilized. This minimizes the reflection from the resist-glass interface. The other end of the glass substrate is coated with anti-reflection coating ( $MgF_2$ ) to minimize the reflection from glass-air interface.

In the resist development model of Dill, et al., development of positive photoresist is considered as a surface-rate limited etching reaction. The parameters that control this rate are resist and developer chemistry. Dill, et al. defined the development behavior as a log-polynomial function of inhibitor concentration with parameters  $E_1$ ,  $E_2$ , and  $E_3$  describing the polynomial:

$$\text{Rate}(M) = \exp(E_1 + E_2 M(x) + E_3 M^2(x)) \quad (5)$$



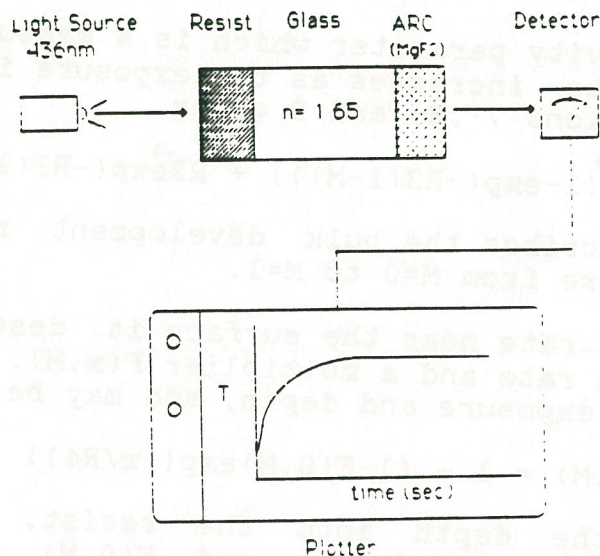


Figure 1 : Schematic diagram of resist optical parameters measurement system.

However, this polynomial fails at high exposure dose. Also, with a significant surface induction effect (the retardation of dissolution rate near the surface compared to the dissolution rate in the bulk), it is necessary to include the depth dependence of development rate in the model.

A model proposed by Neureuther and co-workers includes the retardation of the development rate near the surface, and this is used as a multiplier  $f(x, M)$  to the bulk development rate  $R_b(M)$  [2].

$$\text{Rate}(x, M) = f(x, M) R_b(M) \quad (6)$$

In this product formulation, the depth dependence is independent of  $M$ , thus,  $f(x, M)$  can be separated into individual functions of  $x$  and  $M$ .

The bulk development may be viewed as the dissolution of base resin modified by the presence of photoactive compound, inhibitor, (PAC;  $M$ ), and the dissolution of base resin modified by presence of reacted photoactive compound (carboxylic acid;  $1-M$ ). In order to combine these two dissolution process, Neureuther derived the following form for the rate function  $R$

$$1/R = F_1(M)/R_1 + F_2(M)/R_2 \quad (7)$$

The parameters  $R_1$ , and  $R_2$  are the limiting rates for fully exposed and unexposed resist, respectively. In Equation 7, the first term is associated with resin-carboxylic acid, and the second with resin-PAC dissolutions. The suitable forms for  $F_1(M)$



and  $F_2(M)$  are given by

$$F_1(M) = 1 - \exp(-R_3(1-M)) \quad (8)$$

$$F_2(M) = -\exp(-R_3(1-M)) \quad (9)$$

$R_3$  is a sensitivity parameter which is a measure of how fast the development rate increases as the exposure increases. The combination of Equations 7, 8, and 9 gives

$$R = 1 / R_1(1 - \exp(-R_3(1-M))) + R_2 \exp(-R_3(1-M)) \quad (10)$$

Equation 10 describes the bulk development rate over the full range of exposure from  $M=0$  to  $M=1$ .

The development rate near the surface is described by the product of the bulk rate and a multiplier  $F(x,M)$ . This function is depended on both exposure and depth, and may be written as

$$F(x,M) = 1 - (1 - F(0,M) \exp(-x/R_4)) \quad (11)$$

where  $x$  is the depth into the resist,  $R_4$  is the characteristic retardation depth, and  $F(0,M)$  is the ratio of surface development rate to bulk development rate at any  $M$  value. Neureuther modeled  $F(0,M)$  as a simple linear function of  $M$

$$F(0,M) = R_5 - (R_5 - R_6)M \quad (12)$$

where  $R_5$  is the ratio of surface rate to bulk rate at  $M=0$  and  $R_6$  the ratio at  $M=1$ .

This project was an attempt to obtain optical resist parameters for  $M(x,t)$  determination, and positive resist dissolution rate,  $R(x)$ .

## EXPERIMENT

The apparatus shown in Figure 1 was modified for measuring transmittance of photoresist film due to unavailability of glass substrate with index of refraction of 1.65 and anti-reflection coating. Instead, a glass slide with index of refraction of 1.50 was utilized as the substrate with no anti-reflection coating. The resist was spun at 4000 rpm for 30 seconds and prebaked at 70c for 20 minutes in a convection oven. Monochromatic light (436nm) was used to expose the resist film, and the intensity transmitted through the resist film and the substrate was measured using a radiometer.

The Perkin-Elmer Development Rate Monitor (DRM), model 5900, was used to obtain the dissolution rate of the photoresist. The exposed samples were developed at 20c, with constant agitation. During development, photoresist thickness as function of development time was monitored by the DRM.

Several numerical integration techniques were examined to solve equations 2 and 3 for  $M(x,t)$  and  $I(x,t)$ . Due to the



complexity of these equations, no solution was found.

## RESULTS/DISCUSSION

Table 1 shows both the experimental and literature values of A, B, and C for AZ1350J-SF and KTI820. Figure 2 shows a typical optical transmittance plot for AZ1350J-SF positive photoresist film. Equations 4A, 4B, and 4C have been used to determine A, B, and C values. Due to the absence of a glass substrate with index of refraction of 1.65 and the anti-reflection coating, the values obtained differ from the literature. In addition, problems have been encountered in solving the equations 2 and 3 to determine the inhibitor concentration. Thus, the development rate was not characterized as function of inhibitor concentration.

TABLE 1 : A,B,C Exposure Parameters  
(Prebake 80c,25min;Exposed for 436nm)

Photoresist	A um-1	B um-1	C sec-1
AZ 1350J-SF	0.578	0.020	0.480
(Reported Values)	0.536	0.059	0.411
(Prebake 100c,25min;Exposed for 436nm)			
Photoresist	A um-1	B um-1	C sec-1
KTI 820	0.665	0.062	0.089
(Reported Values)	0.510	0.031	0.013mJ/cm2

Transmittance Versus Exposure Time  
AZ 1350J-SF Positive Photoresist

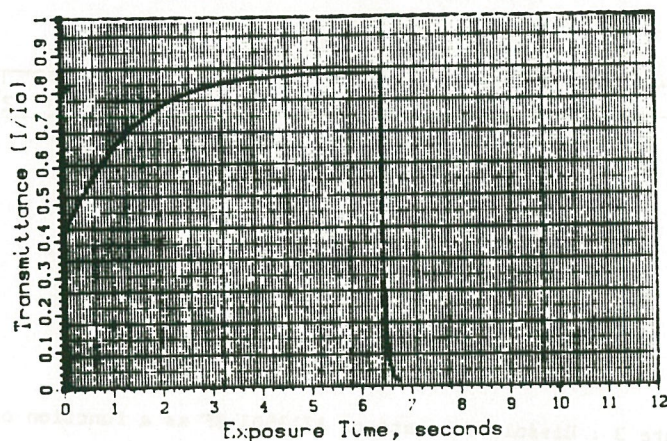


Figure 2 : Optical transmittance of a 1.3um film of AZ1350J-SF resist as a function of exposure time.



Figure 3 shows the dissolution rate as a function of depth for AZ1350J-SF, obtained from the DRM. The development rate retardation near the surface of photoresist, addressed in the Neureuther development model, is apparent.

Shipley 1400-27 positive photoresist has been characterized under various processing conditions. The simulated exposure condition uses a lens with NA=0.28, sigma=0.7, and wavelength of 436 nanometers. The dissolution rates for Shipley MF312, and MF319 developers are compared in Figure 4. MF312 developer showed superior contrast and sensitivity but at the expense of a higher unexposed development rate. The exposure doses were adjusted to yield a 1 micrometer linewidth. The effect of development temperature on resist profile is shown in Figure 5. The development of metal ion free developer unexpectedly decreases with increasing temperature.

Due to the complexity of solving equations 2 and 3, the development rate behavior was not characterized as a function of the inhibitor concentration.

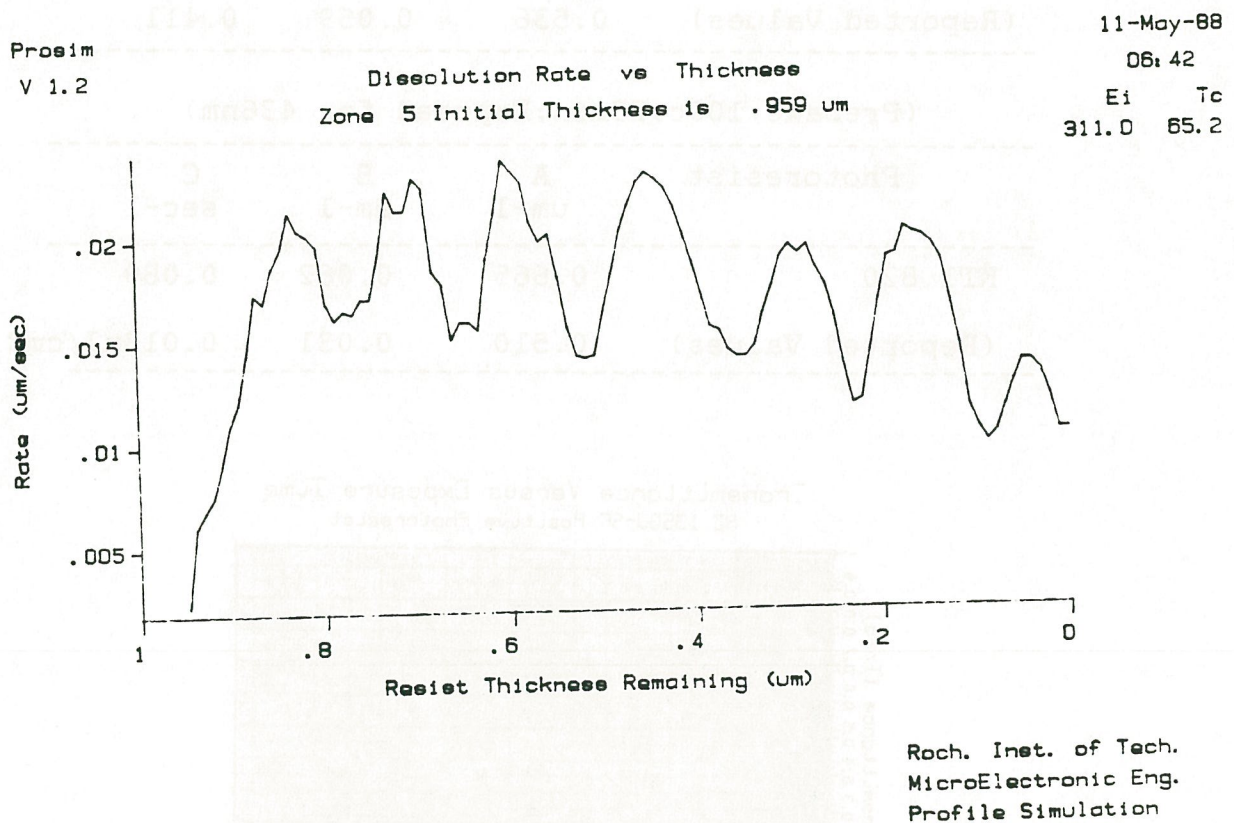
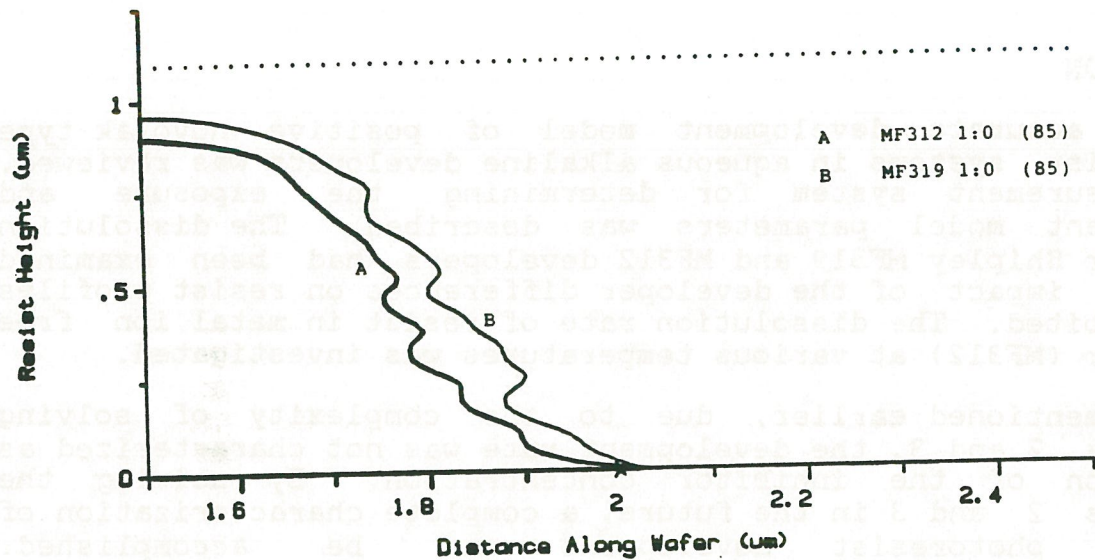


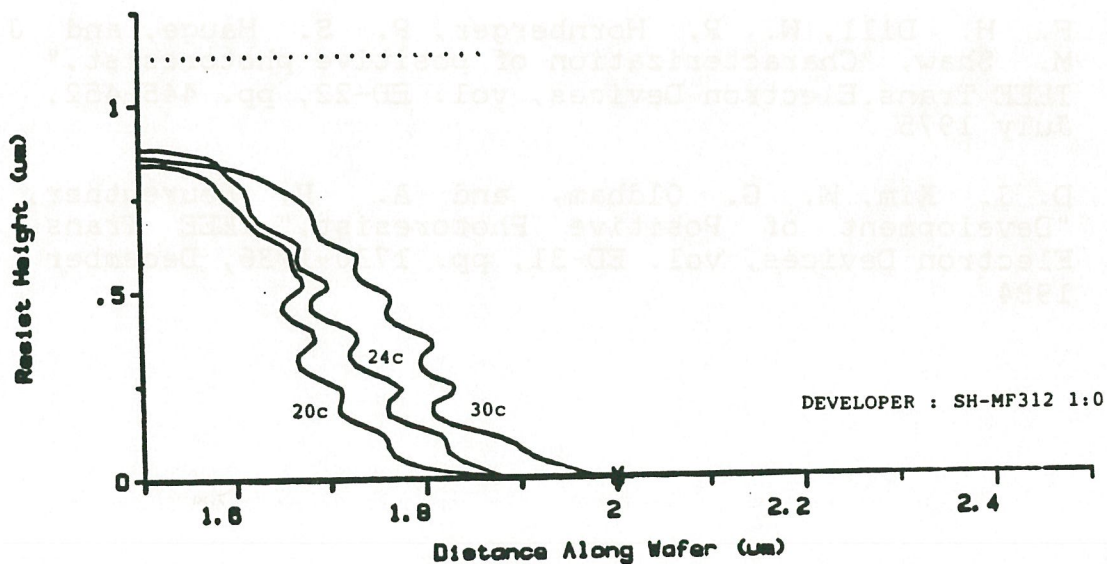
Figure 3 : Dissolution rate of AZ1350J-SF as a function of the thickness.



\*DOSES ARE INDICATED BY ( ) IN mj/cm<sup>2</sup>.

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Figure 4 : Simulation of resist profiles of Shipley 1400-27 resist for 2 different developers. Doses are indicated by ( ) in mj/cm<sup>2</sup>.



EXPOSURE : 135 mj/cm<sup>2</sup>

DEVELOPMENT TIME : 185 seconds

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Figure 5 : Simulation of resist profiles of Shipley 1400-27 for several developer temperatures.



## CONCLUSION

An accurate development model of positive novolak-type photoresist systems in aqueous alkaline developers was reviewed. The measurement system for determining the exposure and development model parameters was described. The dissolution rates for Shipley MF319 and MF312 developers had been examined and the impact of the developer differences on resist profiles was exhibited. The dissolution rate of resist in metal ion free developer (MF312) at various temperatures was investigated.

As mentioned earlier, due to the complexity of solving equations 2 and 3, the development rate was not characterized as a function of the inhibitor concentration. By solving the equations 2 and 3 in the future, a complete characterization of positive photoresist development can be accomplished. Understanding the behavior of resist dissolution is very essential for improving a photolithographic process.

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## REFERENCES

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