Characterization of Positive Photoresist

FREDERICK H. DILL, SENIOR MEMBER, IEEE, WILLIAM P. HORNBERGER, PETER S. HAUGE, MEMBER, IEEE, AND JANE M. SHAW

***Abstract*—This paper presents techniques for measuring a new set of parameters used to describe the image forming properties of positive photoresist [1]. Exposure is described by three optical parameters, *A*, *B*, and *C*, through which the process is modelled. Development is described in terms of a rate relationship *R*(*M*) between the rate of removal of photoresist in the developer and the degree of exposure of the photoresist. This set of functional parameters provides a complete description of positive photoresist exposure and development, and is the basis for the theoretical process models discussed in the accompanying papers.**

POSITIVE PHOTORESIST

POSITIVE acting photoresists, of the type exemplified by the Shipley Company's AZ1350J, are composed of three components: a photoactive compound, a base resin, and a suitable organic solvent system. The patent literature [2] suggests that the structures shown in Fig. 1 are typical of these systems.

In the absence of the photoactive compound, a film composed only of the base resin is moderately soluble in the aqueous alkaline developer usually employed with this system, with a removal rate of about 15 nm/s. When the photoactive compound is present, typically in the amount of 25–30 weight percent, the dissolution rate of unexposed photoresist film is reduced to the range of 0.1–0.2 nm/s. Hence the term "inhibitor" is introduced to emphasize the functional role of the photoactive component inhibiting dissolution. Radiant energy in the wavelength range of 300–450 nm destroys the inhibitor component and results in an *increased* film dissolution rate of up to 100–200 nm/s in the developer system, depending upon the fraction of inhibitor remaining.

Our choice of photoresist characterization parameters has been dictated by the need for the parameters to be useful in theoretical calculations of image profiles resulting from exposure and development of a photoresist film [3],[4]. Any set of parameters sufficient to predict photoresist performance will be sufficient to give quantitative type to type and batch to batch comparisons. They will also allow processing variations to be studied with the aim of process improvement and optimization.

The need to convert optical exposure effects into photoresist surface contours after development has led us to characterization parameters with a strong physical basis and only a weak link to the chemistry of the process. The parameters we use to describe photoresist performance

Manuscript received January 21, 1975; revised March 3, 1975.
The authors are with the IBM Thomas J. Watson Research Center, Yorktown Heights, N. Y. 10598.

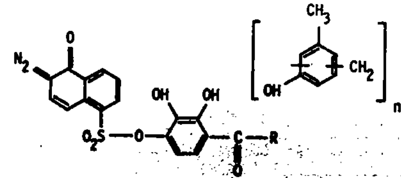

Fig. 1. Chemical structure of a typical positive photoresist.

are thus somewhat remote from the organic and photochemical parameters used by the manufacturer to control his production.

The photoresist process conveniently separates into two distinct parts: exposure and development. Exposure is an optical process which chemically alters the photoresist; development is a surface dissolution process which removes the photoresist at a rate which depends upon the degree of alteration.

For positive photoresist, the absorption of light by the photoactive inhibitor can be used as a tag for this compound. This absorption decreases as the compound is destroyed. The decrease is localized to the immediate region where the destruction occurs. We find that we can describe this behavior in terms of three parameters: A, an exposure absorption dependent term; B, an exposure independent absorption term; and C, an optical sensitivity term. We describe an exposed photoresist film in terms of M, the fraction of inhibitor remaining after exposure relative to that before. The values of A, B, and C are dependent on exposure wavelength; they must be measured over a range of wavelengths to completely characterize the photoresist for exposure by broad band radiation.

Development of positive photoresists under practical conditions can be described as a surface-limited etching reaction. The rate of this reaction is controlled by the resist chemistry, its degree of exposure (M), and the developer chemistry. Holding the resist and developer chemistry constant, we can measure the etching or removal rate, R, as a function of relative inhibitor concentration M. This function, $R(M)$, fully describes the development process for a given resist (composition and processing) and developer (concentration and temperature) chemistry. In general, the rate is only weakly dependent on developer flow-rate or agitation.

RESIST REQUIREMENTS FOR CHARACTERIZATION

The characterization procedure described in this paper is valid only for positive photoresists, and even then with qualifications required to make the resist parameters

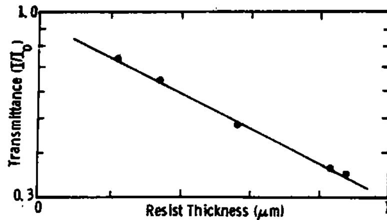

Fig. 2. Optical transmittance of unexposed AZ1350J photoresist as a function of film thickness.

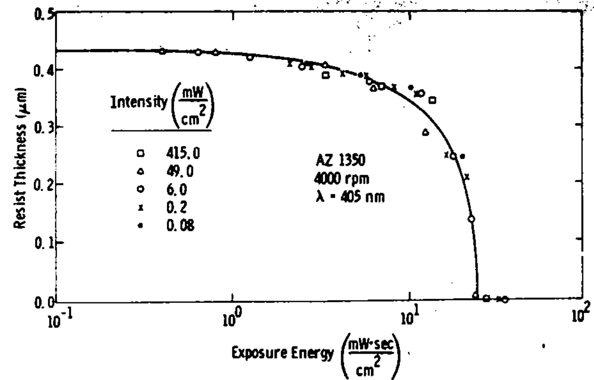

Fig. 3. Resist thickness after development as a function of exposure energy for different values of illumination intensity.

fulfill the assumptions of the theoretical model. These requirements can be met by the positive photoresists we have studied to date provided suitable processing conditions are used.

The photoresist film after application to the substrate and drying must be a uniform isotropic medium. It must have uniform thickness (on both micro and macro scales) over the region used for characterization. It should be chemically isotropic so that its response to exposure and development is uniform throughout the film. Particularly, radial (starburst) thickness variations often associated with the application of photoresist by spinning must be avoided.

Since optical absorption measurements will be an important part of the characterization, several qualifications must be met. Optical scattering must be small so that the material can be described optically by its index of refraction and an absorption coefficient, α. Measurement of the transmittance of unexposed Shipley AZ1350J photoresist films as a function of thickness, as shown in Fig. 2, shows the logarithmic dependence expected from Beer's law and indicates that this assumption is reasonable for this photoresist. The inhibitor must contribute significantly to the optical absorption of the resist at exposure wavelengths. Destruction of the inhibitor must change this absorption in a manner that can be described by a single optical sensitivity term. Although multiple photoactive species have been treated in theory [5], we feel that it is unlikely that more than a single sensitivity term can be derived from practical measurement techniques.

The rate of destruction of the inhibitor must be proportional to the local exposure intensity. This implies exposure reciprocity (the effects of exposure depend on exposure energy), so that intensity and time can be exchanged freely. Fig. 3 shows that the effects of exposure do depend on exposure energy, independent of intensity, for Shipley AZ1350J photoresist [6]. As far as we know, there are no verified deviations from reciprocity for positive photoresists.

For characterization purposes, the photoresist films must be on special glass substrates which closely match the index of refraction n of the photoresist. This is necessary to minimize reflections back into the photoresist from the resist–substrate interface. Such reflections cause coherent optical interference effects which are normally present with resist layers on silicon and significantly complicate any exposure calculations, as is seen in the accompanying papers. Practically, it is only possible to match the real part of the index of refraction, but the extinction coefficient typically is small enough ($k < 0.03$) that this introduces little error as long as n is matched.

For AZ1350J, polished disks of Schott SSKN5 optical glass are used as substrates. These have an index of 1.70 at 404.7-nm wavelength; this matches the resist well. A quarter wavelength coating of MgF_2 is used on the back surface of the substrate to reduce reflection there from nearly 7 percent to under 1 percent. For exposure by anything but a laser source, this back-surface reflection is incoherent, but it is convenient not to have to consider it in the computations.

We postulate that the rate of dissolution of an exposed photoresist film is only a function of the local inhibitor concentration, M. Essentially we have described a surface controlled etching reaction, rate limited by the local concentration of inhibitor, M, at the film–developer interface. We make no *a priori* assumptions as to the detailed chemistry or mathematical form of this development rate relationship, $R(M)$.

Diffusion and swelling at the resist interface, or local changes in developer action due to developer byproducts, could invalidate the surface-limited reaction assumption—so could a chemical reaction rate controlled by the average inhibitor concentration for some distance into the resist, comparable to the variation due to interference effects (50 nm).

Our experimental evidence indicates that the surface-limited rate assumption is valid in the bulk photoresist film. At the original film surface, initiation effects have sometimes been seen. One might postulate such effects near the vicinity of any dielectric discontinuity, e.g., in the vicinity of the substrate–photoresist interface. We have not as yet investigated these aspects in detail, but the model can be extended to include this type of interface effect.

If one pays reasonable attention to recommended processing conditions, many positive photoresists can be characterized using our procedures. Optical scattering is a small effect in most films. Extreme thermal processing conditions can cause failure of the uniformity requirement. Multiple photoactive species could be present in some resists, but we have not seen any evidence of this in resists

thus far studied. Major changes in developer chemistry might invalidate the surface-limited rate assumption, but again we have no problems to date.

The common negative photoresists do not fit this picture at all. Exposure occurs via cross-linking large molecules, not destruction of a single photoactive species. Development usually involves diffusion of developer into the resist and considerable swelling of the resist film. The characterization and modeling of these materials has not been attempted.

OPTICAL ABSORPTION OF POSITIVE PHOTORESIST

For photoresist films on optically matched substrates, the mathematics of exposure is significantly simplified. With light passing through the resist without reflections we can use a Lambert–Beer Law to describe the optical absorption

$$\frac{dI}{dx} = -I\Sigma a_i m_i \tag{1}$$

where

- I the light intensity
- x the distance from the resist–air interface
- m_i the molar concentration of the ith component
- a_i the molar absorption coefficient of the ith component.

For positive photoresists, we need to consider three absorbing species: the inhibitor, the base resin, and the reaction products. Exposure converts inhibitor to reaction products, reducing the total absorption of the film. We use these changes to characterize the photoresist for exposure.

For positive photoresist,

$$\frac{\partial I(x,t)}{\partial x} = -I(x,t)[a_1m_1(x,t) + a_2m_2(x,t) + a_3m_3(x,t)] \tag{2}$$

where

- $I(x,t)$ light intensity at any depth (x) in the film and exposure time (t)
- a_1 molar absorption coefficient of inhibitor
- a_2 molar absorption coefficient of base resin
- a_3 molar absorption coefficient of reaction products
- $m_1(x,t)$ molar concentration of inhibitor
- $m_2(x,t)$ molar concentration of base resin
- $m_3(x,t)$ molar concentration of reaction products.

The destruction of inhibitor is given by

$$\frac{\partial m_1(x,t)}{\partial t} = -m_1(x,t)I(x,t)C \tag{3}$$

where C is the fractional decay rate of inhibitor per unit intensity.

The following auxiliary equations and assumptions are implicit:

$I(0,t) = I_0$	constant lamp intensity (4)
$m_1(x,0) = m_{10}$	initial inhibitor uniformity (5)
$m_2(x,t) = m_{20}$	resin uniformity and constancy (resin does not bleach) (6)
$m_3(x,t) = m_{10} - m_1(x,t)$	1-mole inhibitor → 1-mole reaction product. (7)

Substituting into (2),

$$\frac{\partial I(x,t)}{\partial x} = -I(x,t)[m_1(x,t)\{a_1 - a_3\} + a_2m_{20} + a_3m_{10}]. \tag{8}$$

Normalizing relations,

$$M(x,t) = \frac{m_1(x,t)}{m_{10}} \quad \text{fractional inhibitor concentration} \tag{9}$$

$$A = (a_1 - a_3)m_{10} \quad [A] = L^{-1}\ (\mu\text{m}^{-1}) \tag{10}$$

$$B = (a_2m_{20} + a_3m_{10}) \quad [B] = L^{-1}\ (\mu\text{m}^{-1}) \tag{11}$$

$$C = C \quad [C] = L^2E^{-1}(\text{cm}^2/\text{mJ}). \tag{12}$$

Substituting these into (2) and (3) yields the working equations

$$\frac{\partial I(x,t)}{\partial x} = -I(x,t)[AM(x,t) + B] \tag{13}$$

$$\frac{\partial M(x,t)}{\partial t} = -I(x,t)M(x,t)C. \tag{14}$$

These equations are subject to the following initial conditions (before exposure):

$$M(x,0) = 1 \tag{15}$$

$$I(x,0) = I_0 \exp[-(A + B)x] \tag{16}$$

and boundary conditions (at the resist–air interface):

$$I(0,t) = I_0 \tag{17}$$

$$M(0,t) = \exp(-I_0Ct). \tag{18}$$

Equations (13) and (14) can be solved by straightforward numerical integration techniques for $I(x,t)$ and $M(x,t)$ once A, B, C, and I_0 are specified.

RELATION OF A, B, AND C TO RESIST OPTICAL TRANSMITTANCE

The internal transmittance, T, of a photoresist film on a matched substrate is given generally by

$$T(t) = \exp\left[-\int_0^d \{AM(x,t) + B\}\,dx\right] \tag{19}$$

where d is the resist film thickness. For an unexposed film, this reduces to

$$T(0) = \exp[-(A+B)d] \quad (20)$$

and for a completely exposed film

$$T(\infty) = \exp[-Bd]. \quad (21)$$

The rate of change of transmittance is given as

$$\frac{dT(t)}{dt} = -T(t)\frac{d}{dt}\left[\int_0^d \{AM(x,t)+B\}\,dx\right] \quad (22)$$

$$\frac{dT(t)}{dt} = -T(t)A\int_0^d \frac{\partial M(x,t)}{\partial t}\,dx. \quad (23)$$

At the start of exposure, (14) and (16) can be combined to give

$$\frac{\partial M(x,0)}{\partial t} = -CI_0 \exp[-(A+B)x] \quad (24)$$

so that the initial change in transmittance is

$$\frac{dT(0)}{dt} = T(0)A\int_0^d CI_0 \exp[-(A+B)x]\,dx \quad (25)$$

$$\frac{dT(0)}{dt} = T(0)[1-T(0)]\frac{A}{A+B}I_0C. \quad (26)$$

This leads us to a set of asymptotic relationships for A, B, and C based on the transmittance of a resist film at the beginning of exposure, the initial rate of change of transmittance, and the transmittance when fully exposed.

$$A = (1/d)\ln[T(\infty)/T(0)] \quad (27)$$

$$B = -(1/d)\ln T(\infty) \quad (28)$$

$$C = \frac{A+B}{AI_0T(0)\{1-T(0)\}}\frac{dT(0)}{dt}. \quad (29)$$

MEASUREMENT OF A, B, AND C

The optical transmittance of photoresist films during exposure is easily determined. Fig. 4 shows a typical measurement environment. A uniform monochromatic light beam is used to expose the resist film, and the intensity transmitted through the resist film and substrate is measured using the detector. In practice, we use a calibrated incident-flux meter which can be moved to the position of the resist sample to determine the light intensity incident on the resist film. We generally use a digital computer to acquire and store transmittance data; this is a considerable convenience for calculating and refining A, B, and C values.

The reflectance from the resist–air interface is accounted for by measuring the intensity transmitted through an uncoated glass substrate. Since the glass and the resist have the same index of refraction, they have equal front-surface reflections. Fig. 5 shows the optical transmittance of a 2.2-μm film of AZ1350J photoresist. This measurement was made at a wavelength of 404.7 nm with an incident flux of 0.5 mW/cm².

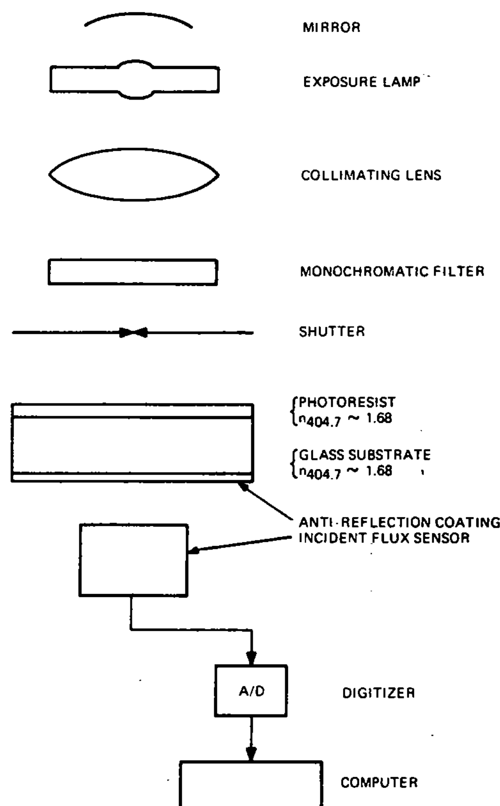

Fig. 4. Exposure environment for characterizing positive photoresist.

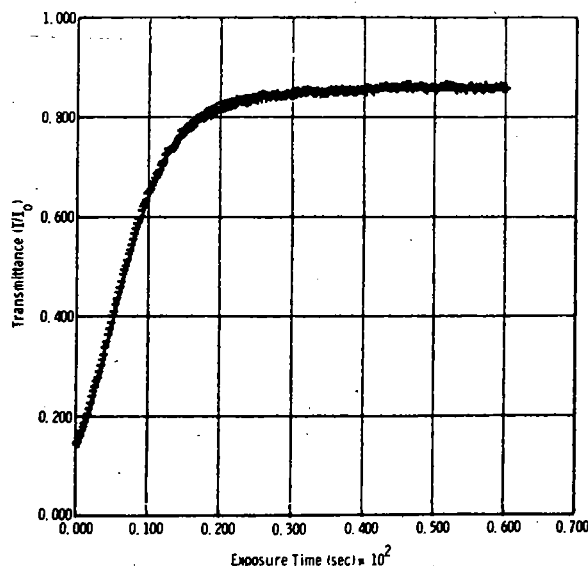

Fig. 5. Optical transmittance of a 2.2-μm film of AZ1350J photoresist as a function of exposure time.

We use (27), (28), and (29) to calculate initial values of A, B, and C. Better values can be calculated using

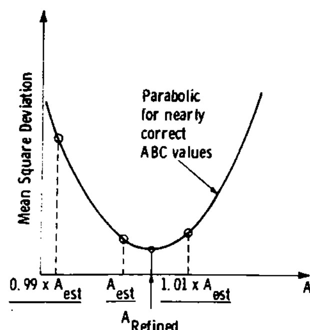

Fig. 6. Mean square deviation as predicted by three estimates of A.

the entire transmittance curve. This is done by a computer program which modifies the estimated A, B, and C values to give a best fit to the transmittance curve. Equations (13) and (14) are used with the initial estimates of A, B, and C and the measured film thickness d to calculate the transmittance of the resist film $T_c(t)$ over the experimental time interval. This is used to find the mean square deviation, MSD, from the experimental curve $T_e(t)$:

$$\text{MSD} = (1/N) \sum_{i=1}^{N} [T_c(t_i) - T_e(t_i)]^2. \tag{30}$$

One variable such as A is incremented and decremented by a small amount such as ± 1 percent, and MSD calculations repeated as is shown in the plot of MSD as a function of A in Fig. 6.

A refined estimate of A is determined by finding the minimum of the parabola drawn through the three calculated points. This new value of A is used with the previous B and C values to obtain a refined value for B. Similarly, the new A and B values are used with the previous C value to refine that term. This refinement is repeated until the MSD is small enough or no longer decreases with repeated calculations. Typically one needs to recalculate A, B, and C values twice to obtain better than 1-percent rms fit, i.e., MSD < 0.0001. The refined values of A, B, and C typically differ from the initial estimates by approximately 5 percent.

These values of A, B, and C together with the real part of the index of refraction can be used as a specification of the exposure properties of a photoresist film for a particular wavelength. Complete specification requires measurement for the wavelengths or wavelength ranges used for practical resist exposure. Table I gives typical values of A, B, and C, and index of refraction n for AZ1350J photoresist at the three principle mercury spectral lines used for exposure.

MEASUREMENT OF THE DEVELOPMENT RATE CURVE

Once we have determined A, B, and C, we can numerically integrate (13) and (14) to determine the inhibitor distribution for similar resist films on matched substrates exposed in our experimental environment for specific lengths of time. Fig. 7 shows normalized inhibitor con-

TABLE I
A,B,C EXPOSURE PARAMETERS FOR AZ1350J PHOTORESIST AT THE PRIMARY MERCURY LINES USED FOR EXPOSURE (70°C, 1-h PREBAKE)

Wavelength (nm)	A (μm^{-1})	B (μm^{-1})	C (cm^2/mJ)	n
435.8	0.54	0.06	0.014	1.68
404.7	0.86	0.07	0.018	1.70
365.0	0.74	0.20	0.012	1.72

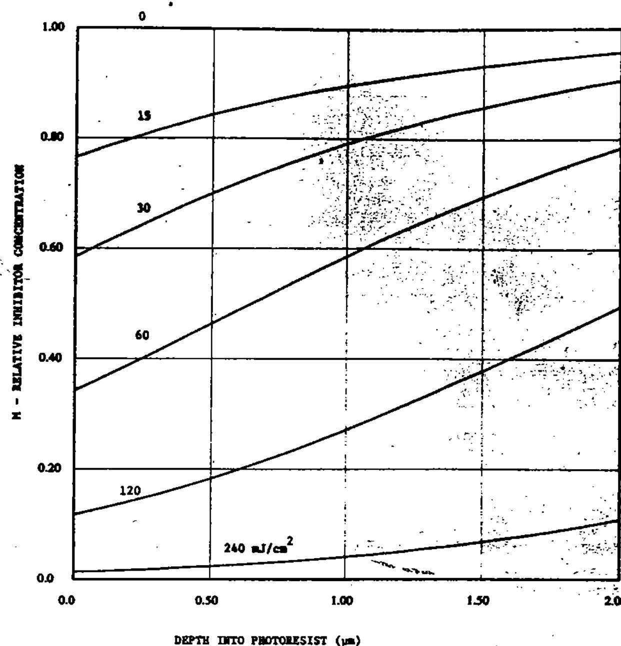

Fig. 7. Relative inhibitor concentration as a function of depth into a photoresist film on a matched substrate for different exposure energies.

centration as a function of distance from the resist–air interface for different total exposure energies. In the matched environment, the inhibitor distribution does not depend upon resist thickness, making these calculations useful for films up to 2 μm.

Note that even for this relatively simple exposure environment, inhibitor concentration is never uniform once exposure has started. With relatively thick films, a considerable exposure (inhibitor concentration) range may be contained within a single photoresist film. Measurement of the development rate of such a film as a function of depth into the film then allows characterization of development for that inhibitor range.

As we said before, we make no assumptions about the form of the relationship between inhibitor and development rate. This relationship is measured during development of films with known inhibitor distribution. Use of the optically matched substrate greatly simplifies calculation of inhibitor distribution; it also, however, makes an optical determination of film thickness during development a challenge.

The development apparatus used is specifically designed to allow *in-situ* resist thickness measurements during

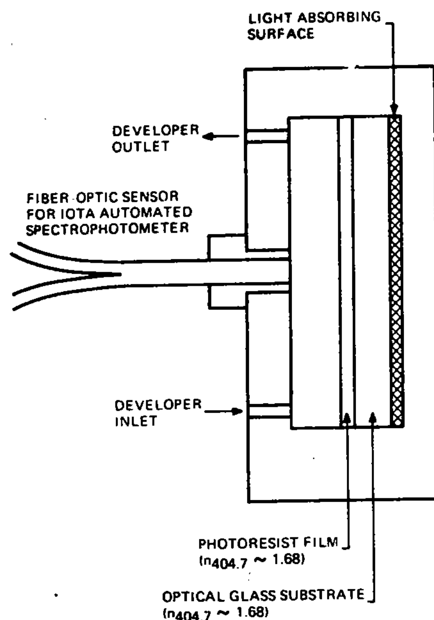

Fig. 8. Development cell used for *in-situ* measurements of photoresist thickness during development.

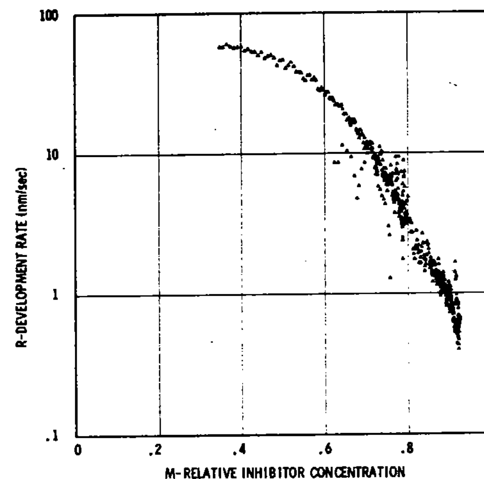

Fig. 9. Development rate curve for AZ1350J photoresist in 1:1 AZ developer: H_2O at 20°C (70°C prebake).

development. The development cell shown in Fig. 8 holds the sample during development. The fiber-optic probe is the sensor for the IOTA scanning spectrophotometer [7] used for thickness measurements. The absorbing surface behind the substrate prevents unwanted reflections. Developer is provided at a controlled and flow rate during the measurement.

Although the substrate has been chosen to be optically matched to the photoresist at exposing wavelengths, sufficient mismatch occurs in the 550–800-nm wavelength range to permit repeated thickness measurements of the resist film during development. The accompanying paper on *in-situ* measurements describes the measurement technique in detail. Typically 200–500 thickness measurements are made of resist thickness during development. Adjacent measured thickness values are subtracted and divided by the time between readings to determine rate, which is then associated with the inhibitor concentration calculated for that location in the resist film.

Two or more resist samples are used to determine an experimental development rate curve as shown in Fig. 9. This curve is for AZ1350J photoresist developer at 20°C. The development rate of unexposed photoresist can be separately measured to get a value for $M = 1$. This is usually done with a resist film on bare silicon, making thickness measurements much easier.

For modeling purposes, we generally need an analytic relationship between inhibitor concentration and rate of removal. We presently are using a least-squares fit to the experimental data of the form:

$$R = \exp\left(E_1 + E_2M + E_3M^2\right). \tag{31}$$

This 3-parameter fit gives good agreement to the experimental curve for high values of M. It often, however, shows an unphysical maximum in rate at some low M value, $M_{\min}$ below which the fit is unreasonable. This can usually be ignored since the development rate for small M values is so high that it can be considered infinite.

RESULTS

A number of photoresist materials have been characterized for their use under typical processing conditions. Table I shows the A, B, and C exposure parameters typical of Shipley AZ1350J photoresist processed with a 70°C prebake before exposure for 1 h. These A, B, and C values represent a characterization of the photoresist as prepared for exposure. Thermal treatment for drying photoresist can alter these values as shown in Table II. Here A, B, and C are measured for 404.7-nm exposure wavelength with prebake temperatures of 70, 100, and 130°C.

The reduction in A indicates that about one-half of the photoactive compound is destroyed by the 100°C bake and over 95 percent by the 130°C bake. The invariance of C indicates that what inhibitor remains is probably the same compound since its sensitivity is unchanged. The increase in B would indicate that the thermal destruction of the photoactive material is different from the optical process. In all three cases, the relative inhibitor concentration at the start of exposure is taken as unity. Thus M has chemical meaning only relative to the state of the photoresist as prepared for exposure. There will be a significant difference in these three samples for any value of M produced by exposure.

Table III shows comparative A, B, and C values for other typical positive photoresist materials. Exposure properties of these resists are seen to vary widely.

In Fig. 9, we have shown the development rate curve, $R(M)$, for AZ1350J photoresist, prebaked at 70°C for 1 h and developed in 1:1 AZ developer: H_2O at 20°C. This curve, like the exposure parameters, is affected by pre-exposure processing. Fig. 10 shows $R(M)$ for the same resist processed under the same conditions except for a 100°C prebake. Developer chemistry is another parameter in the resist description. Fig. 11 shows a $R(M)$ curve for AZ1350J resist under conditions equal to Fig. 9 except

TABLE II
A,B,C EXPOSURE PARAMETERS FOR AZ1350J PHOTORESIST PREBAKED FOR 1 h AT THREE TEMPERATURES (404.7-nm EXPOSURE WAVELENGTH)

Prebake Temperature	A (μm^{-1})	B (μm^{-1})	C (cm^2/mJ)
70°C	0.89	0.077	0.018
100°C	0.48	0.114	0.019
130°C	0.026	0.131	0.019

TABLE III
A,B,C EXPOSURE PARAMETERS FOR TYPICAL HIGH-RESOLUTION PHOTORESISTS (404.7-nm EXPOSURE WAVELENGTH)

Photoresist	Prebake (1 h)	A (μm^{-1})	B (μm^{-1})	C (cm^2/mJ)
AZ1350J	70°C	0.86	0.07	0.018
AZ1350J	100°C	0.48	0.114	0.019
AZ111	70°C	0.510	0.023	0.016
GAF PR207	70°C	1.13	0.14	0.018

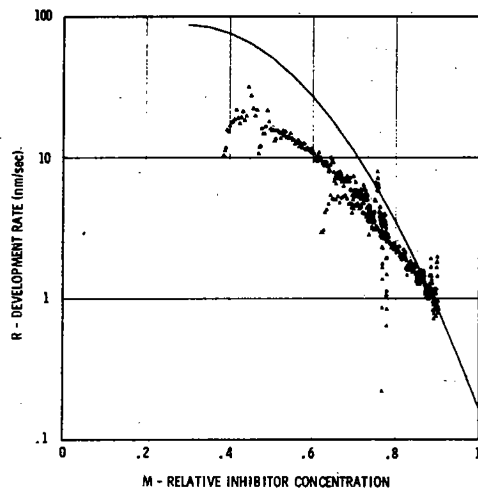

Fig. 10. Development rate curve for AZ1350J photoresist in 1:1 AZ developer: H_2O at 20°C (100°C prebake). Analytic fit to Fig. 9 shown for comparison.

for the use of concentrated AZ developer at 20°C. The fit to Fig. 9 is shown for comparison.

Fig. 12 shows the $R(M)$ curve for Shipley AZ111 photoresist. This is another high-resolution positive photoresist. Prebake was 70°C for 1 h and development in 1:4 AZ303 developer: H_2O at 20°C. It shows significantly less range in its development rate than AZ1350J as shown by the fit to Fig. 9. The range of parameter variation presented in this paper has a significant effect on images made with photoresist—measurement and control of resist performance parameters is just as important as control of other parameters such as exposure and development times, uniformity of exposure illumination, and developer concentration and temperature.

The rate curves shown in Figs. 9–12 can be summarized by the three exponential fit parameters of (31), shown in Table IV. The exponential fit parameters to the $R(M)$ curve, E_1, E_2, and E_3, are not useful for M values less than the M_{min} shown. For M greater than M_{min}, however, the analytic fit is much more convenient than an experimental curve.

TABLE IV
DEVELOPMENT RATE FIT PARAMETERS FOR TYPICAL HIGH-RESOLUTION PHOTORESISTS (21°C DEVELOPMENT TEMPERATURE)

Photoresist	Prebake (1 h)	Developer Dilution	E_1	E_2	E_3	M_{min}
AZ1350J	70°C	1:1	5.63	7.43	−12.6	0.30
AZ1350J	70°C	conc.	2.24	16.92	−15.0	0.55
AZ1350J	100°C	1:1	4.39	5.69	−9.0	0.30
AZ111	70°C	1:1	5.96	−1.19	−2.27	0

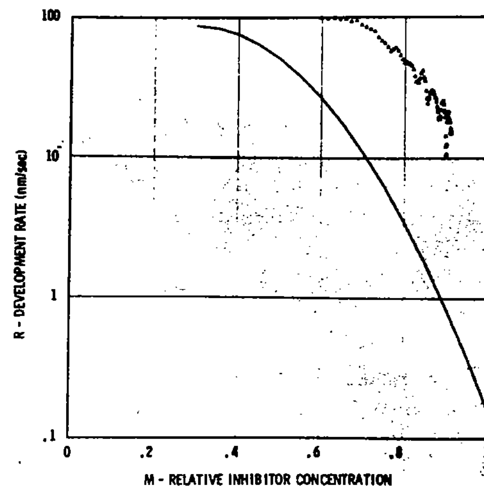

Fig. 11. Development rate curve for AZ1350J photoresist in concentrated AZ developer at 20°C (70°C prebake). Analytic fit to Fig. 9 shown for comparison.

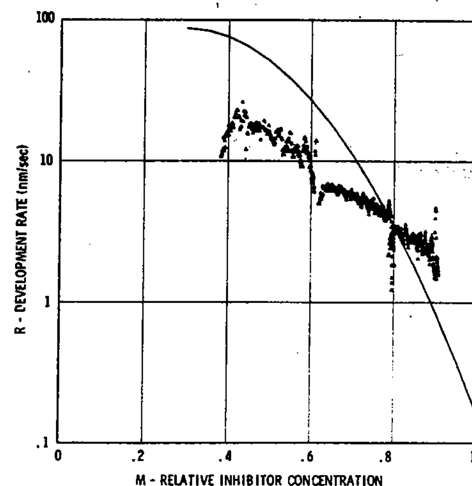

Fig. 12. Development rate curve for AZ111 photoresist in 1:4 AZ303 developer: H_2O at 20°C (70°C prebake). Analytic fit to Fig. 9 shown for comparison.

CONCLUSIONS

The parameters presented in this paper provide an adequate mathematical description of the image-forming properties of positive photoresist; this is demonstrated through their use in photoresist modeling in the accompanying papers. Variation of preprocessing, resist materials, developer type and concentration, exposure time, and development time can result in considerable variation of image-forming performance. With the automated techniques presented, characterization of photoresists can become a routine matter. Used in conjunction

with process models, these measurements become a powerful tool for evaluating potential performance differences given by different resist materials and processes, and their implications for the microelectronics manufacturing industry.

REFERENCES

[1] W. P. Hornberger, P. S. Hauge, J. M. Shaw, and F. H. Dill, "The characterization of positive photoresists," Proc. Kodak Microelectronics Seminar, San Diego, Calif., Oct. 1974.
[2] W. Neugebauer *et al.*, "Etchable reproduction coatings on metal supports," U. S. Patent 3 201 239.
[3] A. R. Neureuther and F. H. Dill, "Photoresist modeling and device fabrication applications," Proc. Microwave Research Institute Symp., Brooklyn, Apr. 1974.
[4] F. H. Dill, J. A. Tuttle, and A. R. Neureuther, "Modeling positive photoresist," Proc. Kodak Microelectronics Seminar, San Diego, Calif., Oct. 1974.
[5] C. E. Herrick, Jr., "Solution of the partial differential equations describing photodecomposition in a light-absorbing matrix having light-absorbing photoproducts," *IBM J. Res. Develop.*, vol. 10, pp. 2–5, Jan. 1966.
[6] M. Schaule, private communication.
[7] K. L. Konnerth and F. H. Dill, "IOTA: A new computer controlled thin film thickness measurement tool," *Solid-State Electron.*, vol. 15, pp. 371–380, 1972.

In-Situ Measurement of Dielectric Thickness During Etching or Developing Processes

KARL L. KONNERTH, MEMBER, IEEE, AND FREDERICK H. DILL, SENIOR MEMBER, IEEE

***Abstract*—A system has been developed which permits the measurement of dielectric film thicknesses *in-situ* during development or etching processes. This can be extended to growth or deposition processes. Two examples of its uses are presented: the determination of the thickness of phosphosilicate glass layers on silicon dioxide coated silicon wafers by making use of the etch rate differences, and the monitoring of photoresist thickness during development to characterize the photoresist development process.**

INTRODUCTION

A CONSIDERABLE amount of information about the properties of thin films can be obtained by measuring the etch rate as a function of depth into the film. This procedure has some particularly important applications in the semiconductor industry. For example, inhomogeneities or boundaries between films of essentially identical optical properties can be located by examining the changes in the rate of etch. Another important application is in the characterization of the etching (developing) processes in photoresist materials.

Until recently, measurement of etch rate was tedious and time consuming. Conventional thickness measurement techniques were too slow to permit *in-situ* measurement of film thickness during the process under investigation. Therefore, such determinations generally used multi-measurement techniques. Either one sample was etched for a short period of time, the thickness measured and the etching and measurement processes repeated, or multiple identical samples were etched for differing periods, then measured. Such procedures are tedious and inaccurate when compared to *in-situ* thickness measurements while etching.

Manuscript received January 21, 1975; revised March 3, 1975.
The authors are with the IBM Thomas J. Watson Research Center, Yorktown Heights, N. Y. 10598.

MEASUREMENT EQUIPMENT AND TECHNIQUE

The instrument used for performing *in-situ* measurements is a computer-controlled spectrophotometer previously described in the literature for static thickness measurements [1]. A brief discussion of the apparatus is presented here; the reader is referred to the literature for a detailed presentation on the equipment as well as the analysis techniques employed.

Fig. 1 shows a block diagram of the spectrophotometer. The heart of the instrument is a circular interference filter whose transmission wavelength is dependent upon its angular position. The 180° filter segment is alternately rotated through two optical paths, thus producing a wavelength scan from 400 to 800 nm in each. During the first 180° of rotation, light from the source is directed through the rotating filter and then to a photomultiplier by means of fiber optics. During the second half of the rotation, another set of fiber optics conducts the light through the filter and onto the sample under investigation. The light reflected from the sample is then channeled to the photomultiplier. By the use of an analog-to-digital converter triggered from the optical encoder on the filter shaft, readings can be obtained of the photomultiplier signal cor-