Absorption and exposure in positive photoresist

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A review of the theory of absorption on microscopic and macroscopic levels is given. This theory is then applied to the absorption of UV light by diazo-type positive photoresist during exposure. A formal treatment of the properties of polychromatic light is given. Using these analyses, the effects of polychromatic exposure of a photoresist are derived. Finally, experimental verification of Beer's law and determination of the exposure quantum efficiency of a particular photoresist is given.

I. Introduction

The phenomenon of absorption can be viewed on a macroscopic or a microscopic scale. On the macrolevel, absorption is described by the familiar Lambert-Beer law which gives a linear relationship between absorbance and path length times the concentration of the absorbing species. On the microlevel, a photon is absorbed by an atom or molecule, promoting an electron to a higher energy state. Both methods of analysis yield useful information needed in describing the effects of light on a photoresist.

If the light used to expose this photoresist is polychromatic, one must be careful to define what is meant by the intensity of light. Usually, intensity is measured by some detector. Different detectors will, in general, give different readings for the intensity of polychromatic light. Thus, a formal definition of the actual intensity must be established along with a method of relating the actual intensity to the measured intensity. Once this has been done, a treatment of the exposure of photoresist by polychromatic light can be similarly formalized.

II. Macroscopic Absorption

The basic law of absorption is an empirical one with no known exceptions. It was first expressed by Lambert in differential form as

$$\frac{dI}{dz} = -\alpha I,\tag{1}$$

where I is the intensity of light traveling in the z direction through a medium, and α is the absorption

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coefficient of the medium and has units of inverse length. In a homogeneous medium (i.e., α is not a function of z), Eq. (1) may be integrated to yield

$$I(z) = I_0 \exp(-\alpha z), \tag{2}$$

where z is the distance the light has traveled through the medium and I_0 is the intensity at z = 0. If the medium is inhomogeneous, Eq. (2) becomes

$$I(z) = I_0 \exp(-abs), \tag{3}$$

where abs = $\int_0^z \alpha(z')dz'$ = the absorbance.

When working with electromagnetic radiation, it is often convenient to describe the radiation by its complex electric field vector. The electric field can implicitly account for absorption by using a complex index of refraction n such that

$$\mathbf{n} = n - iK. \tag{4}$$

The imaginary part of the index of refraction, sometimes called the extinction coefficient, is related to the absorption coefficient by

$$\alpha = 4\pi K/\lambda. \tag{5}$$

In 1852 Beer showed that for dilute solutions the absorption coefficient is proportional to the concentration of the absorbing species in the solution:

$$\alpha_{\text{solution}} = ac,$$
 (6)

where a = molar absorption coefficient;

 $= \alpha MW/\rho;$

MW =molecular weight;

 ρ = density; and

c = concentration.

The stipulation that the solution be dilute expresses a fundamental limitation of Beer's law. At high concentrations, where absorbing molecules are close together, the absorption of a photon by one molecule may affect the ability of another molecule to absorb light. Since this interaction is concentration dependent, it causes

deviation from the linear relation (6). Also, an apparent deviation from Beer's law occurs if the index of refraction changes appreciably with concentration.

For an N component homogeneous solid, the overall absorption coefficient becomes

$$\alpha_T = \sum_{j=1}^N a_j c_j. \tag{7}$$

Of the total amount of light absorbed, the fraction of light which is absorbed by component i is given by

$$\frac{I_{Ai}}{I_{AT}} = \left(\frac{a_i c_i}{\alpha_T}\right),\tag{8}$$

where I_{AT} is the total light absorbed by the film, and I_{Ai} is the light absorbed by component i.

We will now apply the concepts of macroscopic absorption to a typical positive photoresist. A diazonaphthoquinone positive photoresist (such as AZ1350J) is made up of four major components; a base resin R which gives the resist its structural properties, a photoactive compound M (abbreviated PAC), exposure products P generated by the reaction of M with ultraviolet light, and a solvent S. Although photoresist drying during prebake is intended to drive off solvents, thermal studies have shown that a resist may contain 10-20% solvent after a $30-\min 100^{\circ}\text{C}$ prebake.^{2,3} The absorption coefficient α is then

$$\alpha = a_M M + a_P P + a_R R + a_S S. \tag{9}$$

If M_0 is the initial PAC concentration (i.e., with no UV exposure), the stoichiometry of the exposure reaction gives

$$P = M_0 - M. \tag{10}$$

Equation (9) may be rewritten as4

$$\alpha = Am + B,\tag{11}$$

where $A = (a_M - a_P)M_0$; $B = a_PM_0 + a_RR + a_SS$; and $m = M/M_0$.

The quantities A and B are experimentally measurable⁴ and can be easily related to typical resist absorbance curves, measured using an UV spectrophotometer. When the resist is fully exposed, M = 0 and

$$\alpha_{\text{exposed}} = B.$$
 (12)

Similarly, when the resist is unexposed, m = 1 ($M = M_0$) and

$$\alpha_{\text{unexposed}} = A + B.$$
 (13)

From this A may be found by

$$\alpha_{\text{diff}} = \alpha_{\text{unexposed}} - \alpha_{\text{exposed}} = A.$$
 (14)

Thus, $A(\lambda)$ and $B(\lambda)$ may be determined from the UV absorbance curves of unexposed and completely exposed resist (Fig. 1).

III. Microscopic Absorption

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On a microscopic level, the absorption process can be thought of as photons being absorbed by an atom or molecule causing an outer electron to be promoted to a

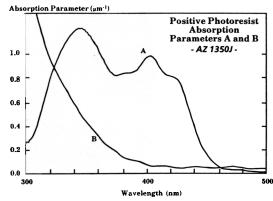


Fig. 1. Photoresist absorption parameters A and B as a function of wavelength for AZ1350J.

higher energy state. This phenomenon is especially important for the photoactive compound since it is the absorption of UV light which leads to the chemical conversion of M to P.

$$M \xrightarrow{\text{UV}} P.$$
 (15)

This concept is stated in the first law of photochemistry: only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule.

Einstein first quantified absorption on a microscopic scale by using probabilities. Consider a substance M being exposed to radiation of intensity I and spectral power density $J(\lambda)$ [where $J(\lambda)d\lambda$ is defined as the intensity of the radiation with wavelengths between λ and $\lambda + d\lambda$ so that $I = \int J(\lambda)d\lambda$, see the following section]. Einstein's relation for photon absorption is⁵

$$\Delta \Phi_{M} = N_{M} B_{E}(\lambda) J(\lambda) d\lambda, \qquad (16)$$

where $\Delta \Phi_M$ = the number of photons with wavelengths between λ and $\lambda + d\lambda$ absorbed per second by M;

 N_M = the number of molecules of M; and $B_E(\lambda)$ = Einstein's coefficient of absorption.

[Originally, Einstein's relation involved an energy density $u(\nu)$ instead of $J(\lambda)$. The original Einstein coefficient B_{nm} is related to $B_E(\lambda)$ by $B_{nm} = B_E(\lambda)c/n$, where c is the speed of light and n is the index of refraction of the medium.] The total number of photons absorbed per second by M at all wavelengths can be found by integrating Eq. (16) over wavelength

$$\Phi_{M} = N_{M} \int_{0}^{\infty} B_{E}(\lambda) J(\lambda) d\lambda. \tag{17}$$

To relate Eq. (16) to measurable quantities, one must relate the microscopic theory to macroscopic observations. Consider an elemental volume containing some amount of substance M (Fig. 2). The light absorbed by the volume (with wavelengths between λ and $\lambda + d\lambda$) is $I_0 - I_T$. The light absorbed by M can be found using Eq. (8):

$$I_{AM} = (I_0 - I_T) \left(\frac{a_M M}{\alpha} \right) \tag{18}$$

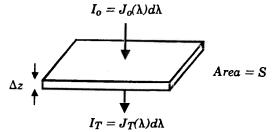


Fig. 2. Geometry used to compare macroscopic and microscopic absorption.

Intensity can be converted to photons absorbed by M per second (between λ and $\lambda + d\lambda$) by

$$\Delta\Phi_{M} = \frac{\lambda S}{hc} \left(I_{0} - I_{T} \right) \left(\frac{a_{M}M}{\alpha} \right), \tag{19}$$

where h is Planck's constant. Now Eqs. (16) and (19) can be equated:

$$\frac{\lambda S}{hc} (I_0 - I_T) \left(\frac{a_M M}{\alpha} \right) = N_M B_E(\lambda) J(\lambda) d\lambda. \tag{20}$$

Dividing both sides of the equation by the volume $S\Delta z$ and by Avogadro's number N_A ,

$$\frac{a_{M}M\lambda}{N_{A}hc\alpha}\left(\frac{I_{0}-I_{T}}{\Delta z}\right)=MB_{E}(\lambda)J(\lambda)d\lambda. \tag{21}$$

Letting Δz go to 0.

$$\lim_{\Delta z \to 0} \left(\frac{I_0 - I_T}{\Delta z} \right) = -\frac{dI}{dz} = \alpha I. \tag{22}$$

Recalling that, in this case, $I = J(\lambda)d\lambda$, Eq. (21) becomes

$$\frac{a_M \lambda}{N_A h c} M J(\lambda) d\lambda = M B_E(\lambda) J(\lambda) d\lambda. \tag{23}$$

Einstein's coefficient of absorption can now be related to the molar absorption coefficient of M:

$$B_E(\lambda) = \frac{a_M \lambda}{N_A h c} \tag{24}$$

Recalling Eqs. (4) and (5),

$$B_E(\lambda) = \left(\frac{4\pi (MW)_M}{\rho_M N_A hc}\right) K_M. \tag{25}$$

Thus, Einstein's coefficient of absorption is proportional to the imaginary part of the index of refraction of the photoactive compound, K_M .

Einstein's coefficient for spontaneous emission $A_E(\lambda)$ can be related to $B_E(\lambda)$ by

$$A_E(\lambda) = \frac{8\pi hc^2n^2}{\lambda^5} B_E(\lambda). \tag{26}$$

Integrating over wavelength gives the overall A_E ,

$$A_E = \frac{8\pi cn^2}{N_A} \int_0^\infty \frac{a_M}{\lambda^4} d\lambda. \tag{27}$$

IV. Polychromatic Light

The light used to expose photoresists is generally in the 300-500-nm wavelength range. Measuring the

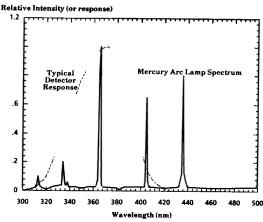


Fig. 3. Typical mercury arc lamp spectrum and a detector response curve.

intensity of the light involves using a detector that invariably does not have a flat response over this range. The question then arises, how does the measured light intensity I_M relate to the actual total intensity I_T for a polychromatic light source? Let us first define a spectral power density $J(\lambda)$ such that

$$I_T = \int_0^\infty J(\lambda) d\lambda. \tag{28}$$

Consider now a hypothetical experiment. The light intensity of some source is measured over a very narrow range of wavelengths between λ_0 and $\lambda_0 + \Delta\lambda$ by inserting a filter with a transmission function $t(\lambda)$ defined as having a transmittance T within the given wavelength range and zero outside the range. Equation (28) becomes

$$I(\lambda_0) = \int_0^\infty t(\lambda)J(\lambda)d\lambda,\tag{29}$$

where $I(\lambda_0)$ is the measured intensity from our hypothetical experiment. If $\Delta\lambda$ is sufficiently small, $J(\lambda)$ can be assumed constant over this range giving

$$I(\lambda_0) = TJ(\lambda_0)\Delta\lambda. \tag{30}$$

The measured $I(\lambda_0)$ is often normalized so that it has a value of 1 at some wavelength. For the case of a mercury arc lamp, one often uses the wavelength $\lambda = 365$ nm. Thus, a relative intensity $I_R(\lambda)$ can be defined:

$$I_R(\lambda_0) = I(\lambda_0)/I(365 \text{ nm}) = J(\lambda_0)/J(365 \text{ nm}),$$
 (31)

where the second equality comes as a result of Eq. (30). A graph of $I_R(\lambda)$ vs λ is known as the spectral output of the light source. Figure 3 shows the spectral output of a typical mercury arc lamp. From Eq. (31), the spectral density $J(\lambda)$ is proportional to this graph:

$$J(\lambda) = I_R(\lambda)J(365 \text{ nm}). \tag{32}$$

Consider now the original problem of relating a measured intensity to the actual intensity. When a detector is used to measure light intensity, Eq. (28) can be modified to read

$$I_{M} = \int_{0}^{\epsilon} S_{D}(\lambda)J(\lambda)d\lambda, \tag{33}$$

where $S_D(\lambda)$ is the spectral response of the detector. Figure 3 shows a typical UV radiometer response curve. Figure 4 shows the product of the two curves in Fig. 3 and can be thought of as the portion of the source output that is seen by the detector. Equation (32) can be used to remove $J(\lambda)$ giving

$$I_{M} = J(365 \text{ nm}) \int_{0}^{\infty} S_{D}(\lambda) I_{R}(\lambda) d\lambda, \tag{34}$$

Solving this equation for J (365 nm) and substituting back into Eq. (32) gives

$$J(\lambda) = \frac{I_M I_R(\lambda)}{\int_0^\infty S_D(\lambda) I_R(\lambda) d\lambda}$$
 (35)

This can now be used in Eq. (28) to give I_T in terms of I_M :

$$I_T = I_M \frac{\int_0^\infty I_R(\lambda) d\lambda}{\int_0^\infty S_D(\lambda) I_R(\lambda) d\lambda}$$
 (36)

Each integral can be evaluated using standard numerical integration techniques and is a constant for a given source/detector system.

One should note that this method of determining I_T is sensitive to variations in the source spectral output I_R . In the example given, only wavelengths near the 365-nm peak are measured due to the narrow response of the detector. If the relative heights of the three major peaks change (due to lamp aging, for example⁶), the measured intensity will not reflect this change. This problem is alleviated by using a detector with a wider spectral range. Obviously, if $S_D(\lambda)$ has a value of one over the range for which $J(\lambda)$ is nonzero, the two integrals in Eq. (36) are equal and I_T will equal I_M .

Equation (36) relates the actual total intensity of light in an isotropic, nonabsorbing medium (such as air) to the measured intensity. If, however, the medium in question is absorbing, I_T is a function of the distance the light has traveled, z, and therefore is dependent on the position of measurement. Equation (28) can be modified to handle this case by letting the spectral density be a function of position as well as wavelength:

$$I_T(z) = \int_0^\infty J(z,\lambda)d\lambda. \tag{37}$$

Consider an absorbing isotropic film in which there are no standing waves (e.g., a very thick film or a film on an optically matched substrate) illuminated by normally incident plane waves. For such a case, we can write

$$J(z,\lambda) = J_0(\lambda)T_{12} \exp[-\alpha(\lambda)z], \tag{38}$$

where T_{12} is the transmittance of the air-film interface and $J_0(\lambda)$ is the incident spectral density, i.e., the source spectral density. Equations (31)-(35) will apply to $J_0(\lambda)$ so that Eq. (36) will become

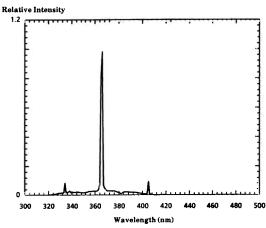


Fig. 4. Part of the mercury arc lamp spectrum that is seen by the detector in Fig. 3.

$$I_{T}(z) = I_{M}T_{12} \frac{\int_{0}^{\infty} \exp[-\alpha(\lambda)z]I_{R}(\lambda)d\lambda}{\int_{0}^{\infty} S_{D}(\lambda)I_{R}(\lambda)d\lambda}$$
(39)

If α is not wavelength dependent, the exponential term can come out of the integral giving the standard integrated form of the Lambert law of absorption:

$$I_T(z) = I_0 \exp(-\alpha z), \tag{40}$$

where

$$I_0 = I_M T_{12} \frac{\int_0^\infty I_R(\lambda) d\lambda}{\int_0^\infty S_D(\lambda) I_R(\lambda) d\lambda}$$

Any similar problem can be solved if a suitable $J(z,\lambda)$ can be defined. For the problem of standing waves caused by exposing a photoresist on a reflecting substrate with a plane wave (e.g., during projection printing), $J(z,\lambda)$ can be defined by⁸

$$J(z,\lambda) = J_0(\lambda) T_{12} \frac{|\exp(-ikz) + \rho_{23} t_D^2 \exp(ikz)|^2}{|1 + \rho_{12} \rho_{23} \tau_D^2|^2} , \qquad (41)$$

where ρ_{ij} is the reflection coefficient between media i and j, k is the propagation constant of the film, τ_D is the internal transmittance of the film, and the subscripts 1,2,3 represent air, resist, and substrate, respectively.

V. Exposure Kinetics

The chemical reaction (15) can be rewritten in general form as

$$M \underset{k_0}{\rightleftharpoons} M^* \xrightarrow{k_3} P, \tag{42}$$

where M = the photoactive compound (PAC);

 M^* = molecule in an excited state;

P =the carboxylic acid (product); and

 k_1,k_2,k_3 = the rate constants for each reaction. Simple kinetics can now be used. The proposed mechanism (42) assumes that all reactions are first order. Thus, the rate equation for each species can be written

$$\frac{dM}{dt} = k_2 M^* - k_1 M,$$

$$\frac{dM^*}{dt} = k_1 M - (k_2 + k_3) M^*,$$

$$\frac{dP}{dt} = k_3 M^*.$$
(43)

A system of three coupled linear first-order differential equations can be solved exactly using Laplace transforms and the initial conditions

$$M(t = 0) = M_0,$$

 $M^*(t = 0) = P(t = 0) = 0.$ (44)

However, if one uses the steady-state approximation the solution becomes much simpler. This approximation assumes that in a very short time the excited molecule M^* comes to equilibrium, i.e., M^* is formed as quickly as it disappears. In mathematical form,

$$\frac{dM^*}{dt} = 0. (45)$$

A previous study has shown that M^* does indeed come to equilibrium quickly, of the order of 10^{-8} s.⁹ Thus,

$$\frac{dM}{dt} = -KM,\tag{46}$$

where

$$K = \frac{k_1 k_3}{k_2 + k_3} \ .$$

Assuming K remains constant with time,

$$M = M_0 \exp(-Kt). \tag{47}$$

The overall rate constant K is a function of the intensity of the exposure radiation. The exact functionality can be determined by analyzing the phenomenon of absorption. In the previous section, an expression was given for the number of photons absorbed by M per second. If we define a quantum efficiency Φ such that

$$P = \frac{\text{molecules of } M \text{ converted to } M^*}{\text{number of photons absorbed by } M}$$
(48)

Eq. (17) becomes

$$\frac{dM^*}{dt} \text{ (generated)} = M \int_0^{\infty} \Phi(\lambda) B_E(\lambda) J(\lambda) d\lambda. \tag{49}$$

But, the rate of generation of M^* is equal to k_1M . Thus,

$$k_1 = \int_0^\infty \Phi(\lambda) B_E(\lambda) J(\lambda) d\lambda. \tag{50}$$

The reverse reaction,

$$M^* \xrightarrow{k_2} M, \tag{51}$$

can occur by three different paths: M^* can spontaneously give off a photon, reverting to M; it can react with some molecule in the photoresist (called quenching); or M^* can undergo induced emission due to the continuing bombardment of photons. The rate constant

 k_2 is the sum of the rate constants of these three mechanisms:

$$k_{2} = A_{E} + k_{q} + \int_{0}^{\infty} B'_{E}(\lambda)J(\lambda)d\lambda, \tag{52}$$

where A_E = Einstein's coefficient of spontaneous emission;

 $B'_{E}(\lambda)$ = Einstein's coefficient of induced emission = $B_{E}(\lambda)$; and

 k_q = rate constant for the quenching reaction. Under normal circumstances (i.e., not a laser) the amount of induced emission is very small. In fact, an order of magnitude analysis using typical resist parameters gives A_E to be 10^8 times greater than $\int B_E(\lambda)J(\lambda)d\lambda$ for a light intensity of 1 mW/cm². Thus, ignoring induced emission and assuming no quenching, the con-

$$k_2 = A_E. (53)$$

The overall rate constant K can now be written as

$$K = \int_0^\infty C(\lambda) J(\lambda) d\lambda, \tag{54}$$

where

stant k_2 becomes

$$C(\lambda) = \frac{k_3 \Phi(\lambda) B_E(\lambda)}{A_E + k_3} \Phi_T(\lambda) B_E(\lambda),$$

and Φ_T is the overall quantum efficiency of the formulation of product P. Equation (47) now becomes

$$M = M_0 \exp \left[-t \int_0^\infty C(\lambda) J(\lambda) d\lambda \right]$$
 (55)

For monochromatic light, this expression simplifies to

$$M = M_0 \exp(-CIt). \tag{56}$$

A study of absorption was used to relate $B_E(\lambda)$ to measurable quantities [Eq. (24)]. This equation can be used to relate the quantum efficiency $\Phi_T(\lambda)$ to measurable quantities:

$$\Phi_T(\lambda) = N_A h c \frac{C(\lambda)}{a_M(\lambda)\lambda} \tag{57}$$

A kinetic analysis of the exposure of a positive photoresist has led to the integrated rate Eq. (55). In deriving this equation we have assumed that $J(\lambda)$ (or I for monochromatic light) was constant within the resist during the exposure. This, however, is not true in general due to the changing chemical composition of the resist as it is being exposed. This problem can be dealt with, however, if I(t) is known. Thus, Eq (55) or (56) forms the backbone of an optical lithography exposure model. Of course, the usefulness of these equations depends on the ability to measure the constant C. Fortunately, a simple experiment can be used to measure C in a straightforward and fairly accurate manner.

When exposing a photoresist, the resist acts as the detector. There is only a certain range of wavelengths to which the resist is sensitive. If we define $S_R(\lambda)$ as the spectral sensitivity of the resist,

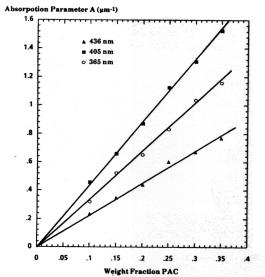


Fig. 5. Verification of Beer's law for an experimental positive photoresist.

$$I_{\rm eff}(z) = \int_0^\infty S_R(\lambda) J(z, \lambda) d\lambda, \tag{58}$$

where I_{eff} is the effective light intensity used by the resist per unit depth into the resist. $S_R(\lambda)$ can be found by a fundamental analysis of the absorption of light, as given above:

$$S_R(\lambda) = \Phi_T(\lambda)a_M(\lambda)M = N_A hcM \frac{C(\lambda)}{\lambda}$$
 (59)

Thus, the sensitivity of the resist is proportional to C/λ and the PAC concentration.

Using the results of the previous section, we can put Eq. (55) in terms of measurable quantities:

$$m = \exp(-C_{\text{eff}}I_M t), \tag{60}$$

where

$$C_{\rm eff} = \frac{\int_0^\infty C(\lambda) I_R(\lambda) d\lambda}{\int_0^\infty S_D(\lambda) I_R(\lambda) d\lambda} \ .$$

Knowing $C(\lambda)$, $S_D(\lambda)$, and $I_R(\lambda)$, the effective constant $C_{\rm eff}$ can be calculated. One should note the similarity between Eqs. (60) and (56). Polychromatic exposure can be treated in a manner identical to monochromatic exposure.

As was mentioned, a technique exists for measuring $C(\lambda)$.⁴ The method involves exposing a photoresist coated glass wafer with light of wavelength λ and measuring the transmitted light with time. Alternatively, if polychromatic light is used, $C_{\rm eff}$ will be measured. Again, this value will be dependent on the particular source/detector combination used to make the measurements.

VI. Experimental Results

As mentioned previously, Beer's law is empirical in nature and, thus, should be verified experimentally.

In the case of positive photoresists, this means formulating resist mixtures with differing photoactive compound to resin ratios. Using Varcum 29-808 resin¹¹ and Fairmount 1010 photoactive compound, 12 photoresists were made with 30% by weight solids content in cellosolve acetate solvent. Of the 30% solids, the PAC to resin weight ratio was varied in different formulations. A total of six formulations were made: 10%, 15%, 20%, 25% 30%, and 35% PAC by weight. Higher percentages of PAC were found to be insoluble at room temperature. The resist mixtures were spin-coated onto quartz wafers to a thickness of ~1 µm and hotplate baked for 3 min at 100°C. The values of the absorption parameters A and B and the exposure rate constant C were measured for each resist at the g, h, and i lines of the mercury spectrum using the technique described by Dill et al.4 The results shown in Fig. 5 show quite clearly a linear dependence of absorption on concentration and extrapolation to zero absorption for zero concentration, in support of Beer's law. The slope of these curves is α_M and is related to a_M by the density and molecular weight of the PAC. Further, using the measured value of C for this resist. the overall quantum efficiency can be determined, as well as $B_E(\lambda)$. These values are given in Table I where the density of the resist was 1.2 g/cm³ and the molecular weight of the PAC was estimated to be 368 g/mol.

Finally, values of the resist absorption parameters A and B and the exposure rate constant C were measured for a variety of commercially available photoresists. The results are shown in Table II.

VII. Conclusions

Two theoretical approaches to absorption by a photoresist have been described. The Lambert-Beer law gives us absorption in terms of measurable quantities. The Einstein relation describes absorption in terms of individual photons, which becomes important when determining a theoretical exposure rate. It has also been shown that these methods of analysis are equivalent, and the Einstein coefficients can be related to measurable quantities found in the Lambert-Beer law. From the point of view of optical lithography, the principles of macroscopic absorption were used in determining the intensity of light in the resist during exposure. The theory of microscopic absorption was used when determining the effects of absorption on resist chemistry.

The problems associated with describing polychromatic radiation can be solved using the methods dis-

Table I. Measured and Calculated Parameters for an Experimental Photoresist

Wavelength (nm)	α _M (μm ⁻¹)	C (cm ² /mJ)	$\Phi_{\mathbf{T}}$	B _E (cm ² /mJ) 0.0316	
365	3.38	0.0118	0.373		
405	4.32	0.0292	0.651	0.0449	
436	2.17	0.0133	0.548	0.0243	

Table II. Absorption and Exposure Parameters for Commercial Photoresists

Resist	365 nm			405 nm			436 nm		
	Α (μm-1)	Β (μm·1)	C (cm ² /mJ)	Α (μm ⁻¹)	Β (μm-1)	C (cm ² /mJ)	Α (μm-1)	Β (μm-1)	C (cm ² /mJ)
AZ1350J	0.955	0.275	0.013	0.934	0.053	0.023	0.579	0.037	0.016
AZ1318sfd	0.898	0.310	0.015	0.949	0.121	0.030	0.573	0.202	0.014
AZ1512	0.916	0.292	0.015	0.917	0.100	0.028	0.556	0.077	0.013
AZ4110	0.512	0.107	0.017	0.468	0.070	0.023	0.266	0.044	0.013
AZ5214	0.563	0.056	0.013	0.517	0.018	0.021	0.029	0.020	< 0.001
Kodak 820	1.000	0.106	0.019	1.045	0.088	0.028	0.563	0.052	0.013
Ultramac PR64	0.982	0.252	0.020	1.026	0.064	0.029	0.536	0.041	0.014
Ultramac PR914	1.032	0.232	0.020	1.036	0.064	0.028	0.601	0.066	0.016
Utramac PR914AR	1.052	0.632	-	1.012	0.775	-	0.592	1.110	•
Shipley 1400-27	1.018	0.271	0.021	1.068	0.061	0.032	0.601	0.066	0.013
Shipley 1400-27D1	0.919	0.357	0.019	0.967	0.153	0.029	0.534	0.252	0.017
Shipley 1813	0.996	0.281	0.019	1.078	0.073	0.036	0.592	0.059	0.015
OFPR-800	0.812	0.284	0.016	0.772	0.105	0.019	0.475	0.073	0.011
OFPR-800 AR-15	0.768	0.384	0.015	0.932	0.224	0.029	0.606	0.241	0.016
EPR-5000	0.909	0.306	0.014	0.971	0.088	0.026	0.563	0.076	0.014
HPR 204	1.189	0.216	0.020	1.162	0.053	0.032	0.655	0.036	0.015
HPR 256	1.015	0.322	0.025	1.058	0.097	0.031	0.517	0.094	0.012
HPR 1182	0.787	0.157	0.018	0.802	0.035	0.027	0.458	0.031	0.014
Xanthochrome	0.639	0.597	-	0.824	0.096	0.028	0.520	0.057	0.016

cussed above. One must know the spectral output of the illumination source and the spectral response of the detector in order to relate the measured intensity (detector reading) to the actual intensity. If one also knows the wavelength dependence of a photoresist exposure rate constant C, the process of exposure can be treated in a straightforward manner. The constant C can be related to other physical properties of the resist or can be measured experimentally.

The results of the above analysis have been incorporated into an overall lithography model called PRO-LITH (the positive resist optical lithography model) which can model polychromatic exposure of photoresist, for example, during contact printing.¹⁰

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References

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 D. A. Skoog and D. M. West, Fundamentals of Analytical Chemistry (Holt, Rinehart, & Winston, New York, 1976), pp. 509-510.

- J. M. Koyler et al., "Thermal Properties of Positive Photoresist and Their Relationship to VLSI Processing," in Proceedings, Kodak Microelectronic Interface '79 (Oct. 1979), pp. 150-165.
- J. M. Shaw, M. A. Frisch, and F. H. Dill, "Thermal Analysis of Positive Photoresist Films by Mass Spectrometry," IBM J. Res. Dev. 21, 219 (1977).
- F. H. Dill et al., "Characterization of Positive Photoresist," IEEE Trans. Electron Dev. ED-22, 445 (1975).
- W. J. Moore, Physical Chemistry (Prenctice Hall, Englewood Cliffs, NJ, 1972), pp. 753-755.
- G. Bachur, "Development of Optical Measurement and Control Systems for Photolithography," Proc. Soc. Photo-Opt. Instrum. Eng. 80, 2 (1976).
- A. Minvielle and R. Rice, "Spectral Output Variations in Perkin-Elmer Micraligns," in Proceedings, Kodak Microelectronic Interface '79 (Oct. 1979), pp. 60-65.
- 8. C. A. Mack, "Analytical Expression for the Standing Wave Intensity in Photoresist," Appl. Opt. 25, 1958 (1986).
- J. Albers and D. B. Novotny, "Intensity Dependence of Photochemical Reaction Rates for Photoresists," J. Electrochem. Soc. 127, 1400, (1980).
- C. A. Mack, "PROLITH: A Comprehensive Optical Lithography Model," Proc. Soc. Photo-Opt. Instrum. Eng. 538, 207 (1985).
- 11. Reichhold Chemicals, Inc., Warren, NJ 07060.
- 12. Fairmount Chemical Co., Inc., Newark, NJ 07105.