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Optical Characterization of i-Line Photoresist

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In recent years, significant advances have been made in the formulation of a number of positive photoresists. Sophisticated photoresists are the backbone of IC manufacturers, because without them today's submicron geometries in the semiconductor industry would be impossible.

At a Glance

The authors have characterized the optical properties of a positive i-line photoresist for 632.8 nm light from a HeNe laser.

Positive photoresist typically consists of three components: a novolac resin, a photoactive compound that is usually a naphthoquinone diazide ester, and a solvent. Occasionally, a dye or other additive is added to improve the latitude of the photolithographic process. These resists must be thermally stable to withstand high-temperature environments such as plasma etching or ion implantation. They must also possess other characteristics including good adhesion with the underlying film, sufficient photospeed, low particulate level, and high contrast. Absorption of light by the photoresist is a critical factor to consider when setting up a photolithographic process. The standard Beer's law of exponential decay can be used to calculate the attenuation of light intensity at any wavelength within the photoresist.[1-3] Owing to the complex nature of positive photoresist, it is imperative that both absorption and scattering be considered when evaluating optical properties of photoresists. Unfortunately, Beer's law cannot separate the attenuation of light intensity by absorption from the actual loss of light by scattering.

Ultraviolet light is routinely employed to expose positive photoresist. During the photolithographic process, UV light is expected to be absorbed strongly by the photoresist, while the longer visible light should have negligible absorption. Therefore, in this paper, we present an in-depth characterization of optical properties of a positive i-line photoresist at 632.8 nm from a HeNe laser. We also compare these results with those obtained on a positive g-line photoresist.[4] The optical properties investigated include absorption and scattering coefficients, total attenuation coefficient, and scattering anisotropy factor. The information on these optical properties can be obtained from the solution of the Chandrasekhar's radiative transport equation describing the rate of change in the intensity of a narrow incident light beam as a function of the optical properties of the medium involved.[5] This is a difficult problem to solve analytically for any turbid media such as positive photoresist. Nevertheless, by assuming homogeneity and regular geometry of the medium, an estimate of light intensity distribution can be obtained by solving the radiative transport equation:

$$\frac{dI}{ds}(r,s) = -(\mu_a + \mu_s)\, I(r,s) + \frac{\mu_a + \mu_s}{4\pi} \int_{4\pi} p(s,s')\, I(r,s')\, d\Omega' \qquad (1)$$

where $I(r,s)$ is the intensity per unit solid angle at target location r in the direction s (s is the directional unit vector), μ_a and μ_s are the absorption coefficient and scattering coefficient, respectively, of the medium, $p(s,s')$ is the phase function representing scattering contribution from the direction s' to s, and Ω' is the solid angle.

The first term on the right-hand side of Equation 1 represents the loss in $I(r,s)$ per unit length in direction s due to absorption and scattering. The second term denotes the gain in $I(r,s)$ per unit length in direction s due to scattering from other scattered light $I(r,s')d\Omega'$ (i.e. light intensity confined in the elemental solid angle $d\Omega'$) from direction s'. The functional form of the phase function in turbid media is usually unknown. In many practical applications, however, the following Henyey-Greenstein formula provides a good approximation of the phase function, and therefore is used in all calculations of the Inverse Adding-Doubling (IAD) method employed in the present study:

$$p(v) = \frac{1}{4\pi} \frac{1 - g^2}{(1 + g^2 - 2gv)^{3/2}} \qquad (2)$$

where ν is cosine of the angle between *s* and *s*′. The Henyey-Greenstein phase function depends only on the scattering anisotropy factor *g*, which is defined as the mean cosine of the scattering angle:

$$g = \frac{\int_{4\pi} p(\nu)\nu d\Omega'}{\int_{4\pi} p(\nu) d\Omega'} \quad (3)$$

The value of *g* ranges from -1 for complete backward scattering to zero for the absolute isotropic scattering to 1 for the complete forward scattering.

Although the radiative transport theory gives a more adequate description of the distribution of photon intensity in the turbid medium than does any other model, the general analytical solution is not known yet. Approximate solutions are only available for such restricted conditions as uniform irradiation, or when either absorption or scattering strongly dominates. Although the general solution is not available, it has been possible in recent years to obtain elaborate computational solution of the transport equation.

To solve Equation 1 , knowledge of absorption and scattering coefficients, and scattering phase factor (or scattering anisotropy factor), is needed. Therefore, appropriate experimental methods are necessary to measure these optical parameters. As an example, although a single measurement of the total transmission through a sample of known thickness provides an attenuation coefficient for the Lambert-Beer law of exponential decay, it is impossible to separate the loss due to absorption from the loss due to scattering. This problem, to some extent, had been resolved by the one-dimensional, two-flux Kubelka-Munk model[6] that has been widely used to determine the absorption and scattering coefficients of turbid media, provided the scattering is significantly dominant over the absorption.

In the past, researchers have applied the diffusion approximation to the transport equation to study turbid media.[7-10] Most notably, following the Kubelka-Munk model and diffusion approximation, an excellent experimental method has been described by van Gemert et al for determining the absorption and scattering coefficients and scattering anisotropy factor.[11,12] Unfortunately, the diffusion approximation, coupled with the Kubelka-Munk method, is valid only when the absorption coefficient is negligibly small compared with the scattering coefficient of the turbid medium under investigation. The scattering coefficient of the positive i-line photoresist is significantly higher than the absorption coefficient at the wavelength of our interest; therefore, the IAD method has been employed to determine both the absorption and scattering coefficients.

In recent years, the IAD method[13] and Monte Carlo simulation technique[14-16] have been successfully used to obtain information on such fundamental optical properties as absorption and scattering coefficients, and scattering anisotropy factor of turbid media. These methods provide by far the most accurate estimates of optical properties than do any other models previously used. Two dimensionless quantities used in the entire process of IAD are albedo, *a*, and optical depth, τ, which are defined as

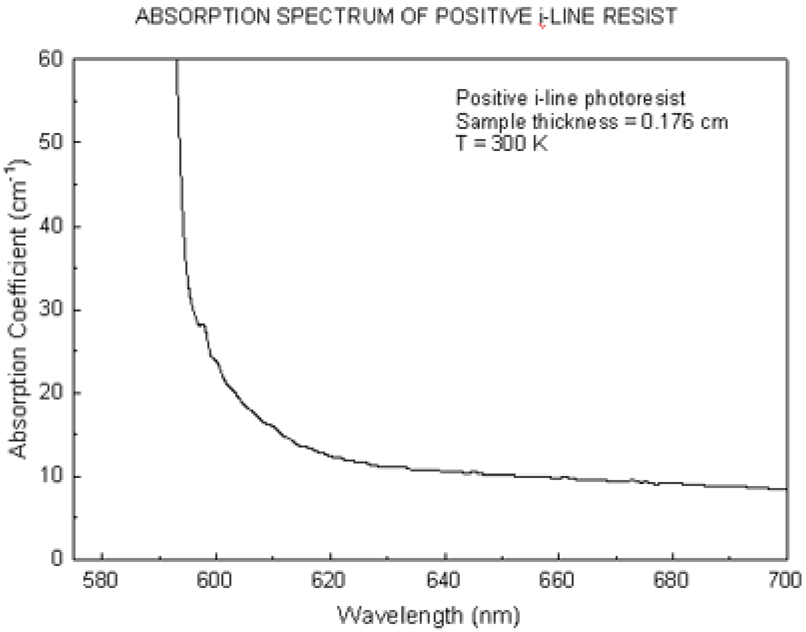
$$a = \mu_s / (\mu_s + \mu_a), \quad \text{and} \quad \tau = t(\mu_s + \mu_a) \quad (4)$$

where *t* is the physical thickness of the sample and measured in centimeters.

The measured values of the total diffuse reflectance and transmittance, using an integrating sphere and unscattered collimated transmittance, have been applied to the IAD method to determine the absorption and scattering coefficients, and scattering anisotropy factor of the positive photoresist sample. Employing this method, these optical properties are obtained by repeatedly solving the radiative transport Equation 1 until the solution matches the measured values of the diffuse reflectance and diffuse transmittance, and collimated transmittance.

Materials and methods

The positive i-line photoresist used in this study was Shipley Megaposit SPR 220-4.5, supplied by Microchem Corp. (Newton, Mass). According to the material safety data sheet supplied by Shipley Co. LLC (Marlborough, Mass.), the composition of the photoresist consists of the following compounds and their percentage range: ethyl lactate, 30.00-52.00%; anisole, 15.00-25.00%; diazo photoactive compound, 1.00-10.00%; cresol novolak resin, 14.00-40.00%; cresol, 0.01-0.99%; 2-methyl butyl acetate, 1.00-5.00%; n-amyl acetate, 2.00-7.00%; and organic siloxane surfactant, 0.01-0.10%. Preparation of the photoresist sample for the optical measurements involved fixing an o-ring with a diameter of 1 in. between two glass slides; the o-ring acts as a reservoir to retain the liquid sample. The photoresist mixture was then transferred with a pipette into the reservoir for investigation. The sample thickness in this case is the thickness between the glass slides and was measured to be 0.176 cm.



1. The room-temperature absorption spectrum of a positive i-line photoresist.

The room-temperature absorption spectrum of the positive i-line photoresist sample was measured in the visible range using a Cary-14 spectrophotometer upgraded by OLIS and shown in Figure 1. Before taking the absorption spectrum on this sample, a baseline was set to correct the measured spectrum due to Fresnell reflection losses of ~5% and any marginal wavelength-dependent scattering that might occur. The absorption spectrum was corrected for those losses by subtracting the baseline from the measured data. The beam dimension of the light in the Cary-14 spectrophotometer was ~4 × 8 mm

The index of refraction of the positive photoresist was measured by the method of minimum deviation using a hollow quartz prism. The equilateral, hollow prism was made of 1 × 2 cm quartz slides obtained from NSG Precision Cell Inc. (Farmingdale, N.Y.). The method of minimum deviation to determine the index of refraction, n, which is based on Snell's law, provides the following expression for n:

$$n = \frac{\sin\left(\frac{A+\delta_m}{2}\right)}{\sin\left(\frac{A}{2}\right)} \qquad (5)$$

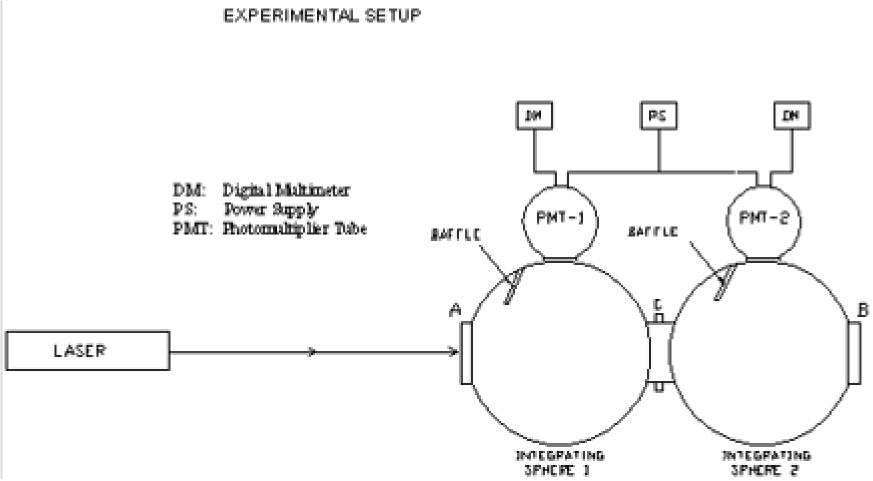
where A is the prism angle and δ_m is the angle of minimum deviation. The index of refraction measurement was repeated three times on the photoresist sample. The experimental details can be seen in Reference 4.

Using an independent experimental technique, the scattering anisotropy factor, g, of the photoresist can also be obtained from the measurements of scattered light intensities (I) at various scattering angles (*U*) using a goniometer table. The scattering anisotropy factor, g, is given by the average cosine of the scattering angle *U* according to the following expression:

$$g = \frac{\sum_i (\cos \theta_i) I_i}{\sum_i I_i} \quad (6)$$

where the sums are taken over all values, *i*, of the scattering angles and intensities. The scattering anisotropy factor obtained by this measurement was compared with that from the IAD method. Experimental details can be seen in Reference 4.

The total diffuse reflectance and transmittance measurements were taken using double integrating spheres (Oriel model 71400). The photoresist sample was placed in a specially designed holder mounted to one of the ports of the integrating sphere. The sample holder was fabricated in the University of Texas at San Antonio Engineering Machine Shop. The light source used for these measurements was a HeNe laser. The maximum power of the HeNe laser, model LHRP-0501 from PMS Electro-Optics, was 10 mW, the beam diameter at $1/e^2$ was 3 mm, and the beam divergence was 0.70 mrad at 632.8 nm.



2. Schematic of the experimental setup for the measurements of diffuse transmittance T_d and diffuse reflectance R_d using double integrating spheres.

The schematic of the experimental setup employed to measure the total diffuse reflectance and total diffuse transmittance is shown in Figure 2. The laser beam was directed into the entrance port A of integrating sphere 1, whose exit port is coupled with the entrance port of integrating sphere 2; the sample to be studied was mounted at C. To achieve a clean laser beam, an iris of 3 mm was placed in front of the entrance port A. The exit port B of integrating sphere 2 was covered with a cap with a reflective surface identical to that of the integrating spheres. The diameter of each sphere was 6 in. and each port has a diameter of 1 in. Light leaving the sample was reflected multiple times off the inner surfaces of the spheres. Reflecting baffles within the spheres shielded the ORIEL model 7068 photomultiplier tubes (PMTs) from direct emission from the sample. Port A was equipped with a variable aperture so that the beam diameter could be appropriately controlled. The reflected and transmitted light intensities were detected by the PMTs attached to the respective measuring ports. The PMTs were powered by a Bertan model 215 high-voltage power supply. Signals from the PMTs were sent to the digital multimeters (Fluke 77, Series II). The measured light intensities were then used to determine the total diffuse reflectance R_d and total diffuse transmittance T_d by the following expressions:

$$R_d = \frac{X_r - Y}{Z - Y} \quad (7)$$

and

$$T_d = \frac{X_t - Y}{Z - Y} \quad (8)$$

where X_r is the intensity detected by the PMT with the sample at B, X_t is the intensity detected by the PMT with the sample at A, Z is the intensity detected by the PMT with no sample at A and a reflective surface at B, and Y is the correction factor measured by the PMT with no sample at A and no reflective surface at B.

The unscattered collimated transmittance T_c was measured to determine the total attenuation coefficient. The collimated laser beam intensities were measured by placing the integrating sphere ~2 m from the sample so that the photons scattered off the sample would be prevented from entering the small aperture (~3 mm in diameter) at the entrance port A. The sample was placed perpendicular with respect to the incident laser beam.

The collimated transmittance T_c was calculated by the relation

$$T_c = \frac{X_c}{Z_c} \quad (9)$$

where X_c is the collimated light intensity and Z_c is the incident light intensity.

From the Beer-Lambert Law, the total attenuation coefficient can be determined from the following expression:

$$\mu_t = \frac{\ln(1/T_c)}{t} \quad (10)$$

where t is the physical thickness of the sample and measured in centimeters.

IAD method

We have used a numerical algorithm known as the IAD method, which was originally developed by Scott Prahl of the Oregon Medical Laser Research Center[13] to determine the optical properties of biological materials. To solve the radiative transport equation, the IAD algorithm must be supplied with experimentally determined values for the total diffuse reflectance (R_d), total diffuse transmittance (T_d), and total collimated transmittance (T_c). The IAD algorithm iteratively chooses values for the dimensionless quantities: albedo, a, and the optical depth, τ, defined in Equation 4 and then adjusts the value of the scattering anisotropy factor, g, until it matches the experimental values of R_d, T_d and T_c. The computed values for the albedo, a, and optical depth, τ, are then used to calculate the absorption and scattering coefficients, μ_a and μ_s, respectively.

Monte Carlo simulation

The accuracy of our measurements of the total diffuse reflectance (R_d) and total diffuse transmittance (T_d), employed in the IAD method to determine the absorption and scattering coefficients, was verified by the Monte Carlo (MC) simulation technique. The MC simulation uses the stochastic model to simulate light interaction in turbid media. The values for μ_a and μ_s calculated by the IAD method, along with the experimentally determined values for the index of refraction n and scattering anisotropy factor, g, are used to compute values for R_d and T_d. Fifteen simulations were run and the results were averaged. These values were then compared for accuracy with the experimentally determined values for R_d and T_d and are given in Table 2 . A detailed theoretical description of the MC model is given in Jacques and Wang.[16]

Results and discussion

The room-temperature absorption spectrum taken on the positive i-line photoresist sample between 575 and 700 nm on the Cary-14 is shown in Figure 1. The spectrum clearly shows that the absorbance of the photoresist sample is extremely high below 600 nm and into the UV region, while it is significantly small above 625 nm. Using the absorption spectrum (Fig. 1), the absorption coefficient of the i-line photoresist at 632.8 nm is determined to be 11.06 cm^{-1}. This value is comparable to the total attenuation coefficient of 9.53 cm^{-1} obtained from the measurement of the collimated transmittance, T_c (Eq. 10). The value of the total attenuation coefficient of the i-line photoresist is significantly higher than that of the g-line photoresist because of the significant differences in their composition.[4]

The index of refraction of the positive photoresist sample was measured using the hollow quartz prism and a HeNe laser and found to be ~1.60. This value is only 1.8% smaller than that reported by Shipley. This measurement was repeated three times, and the values of index of refraction agreed to within 2%. This value of refractive index was used in all subsequent calculations. However, the index of refraction of the g-line photoresist was found to be 1.64.[4]

The total diffuse reflectance and diffuse transmittance were measured on the positive photoresist sample using 632.8 nm light from a HeNe laser. These measurements were repeated three times and the data were found to be in excellent agreement. These values, along with the measured value of the index of refraction of the photoresist sample, were input into the IAD program to obtain the values of the absorption and scattering coefficients, and the scattering anisotropy factor. These values are tabulated in Table 1. The total attenuation coefficient obtained from the IAD method was found to be 10.90 cm^{-1}, which lies between the values obtained by the collimated transmittance (9.53 cm^{-1}) and the Cary-14 spectrophotometer (11.06 cm^{-1}). This discrepancy can be attributed to the fact that the IAD algorithm employed in this study is very sensitive to the measured reflectance data, which was small and found to be only 0.068. A similar discrepancy was observed in the case of g-line photoresist.[4]

Table 1. R_d, T_d, T_c, a, t, μ_a, μ_s, μ_t for Positive i-line Photoresist at 632.8 nm

Experimental			IAD				
R_d	T_d	T_c	a	t	μ_a	μ_s	μ_t
0.068	0.767	0.124	0.906	1.97	1.03	9.87	10.90

The scattering coefficient is found to be much larger than the absorption coefficient at the HeNe laser wavelength of 632.8 nm for the positive i-line photoresist investigated. This can be attributed to the complex composition of the i-line photoresist. The scattering anisotropy factor was determined to be ~0.95 by the scattering experiment. It therefore indicates that the scattering is mostly forward scattering. It is also imperative to include the photon diffusion coefficient of the photoresist medium, which can be determined by the following formula[17]:

$$D = c/3(\mu'_s + \mu_a) \quad (11)$$

where c is the speed of light and μ'_s is the reduced (transport) scattering coefficient defined by $\mu'_s=(1-g)\mu_s$, which is calculated to be 0.494 cm^{-1}. The value of the photon diffusion coefficient is found to be 6.56 × 10^9 cm^2/sec. The transport mean free path (penetration depth) of a photon in the photoresist sample investigated can be defined as $l_t=(\mu'_s+\mu_a)^{-1}$, and is found to be 0.656 cm.

The measured values of the total diffuse reflectance and diffuse transmittance have been verified by the Monte Carlo simulation technique. These values are given in Table 2 . The experimental and Monte Carlo values for the diffuse transmittance differed by <15%, while the values for the diffuse reflectance varied by ~30%. This discrepancy can be attributed to the significantly low intensity of the diffuse reflected light; the reflectance measurements appeared to be very sensitive and susceptible to the experimental errors, thereby leading to the large variation between the measured R_d and that obtained by the MC method.

Table 2. R_d and Td, for Positive i-line Photoresist at 632.8 nm (g=0.95)

Experimental		Monte Carlo	
R_d	T_d	R_d	T_d
0.068	0.767	0.046	0.881

The values of the optical properties reported in this paper can be of significant importance to the semiconductor industry. The optical properties are critically important for photoresist manufacturers and process engineers in order for them to be able to characterize and model photolithographic processes. More importantly, absorption and scattering of laser light from a HeNe laser by a photoresist are important parameters to consider with respect to target recognition on a stepper. This is because most steppers in IC fabrication facilities use a HeNe laser light source for target recognition and alignment of semiconductor wafers.

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