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Optical Characterization of Positive Deep UV Photoresist

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At a Glance

This is the third article of a continuing series on optical properties of positive photoresists. The first article focused on a g-line photoresist, and the second on an i-line photoresist. Our latest research is on the characterization of a positive DUV resist, taking the absorption spectrum on this sample from 250 to 650 nm.

To keep up with the demand for high-quality ICs, wafer fabs have relied on complex semiconductor processing equipment and materials. Deep ultraviolet (DUV) lithography uses light in the 200-300 nm spectral region. In recent years, significant advances have been made in the formulation of a number of positive photoresists; DUV photoresist is one of the most important photoresists used by IC manufacturers. For geometries below 0.5 µm, positive DUV photoresist is particularly useful compared with g-line and i-line resists; this is due to the inverse relationship between resolution and exposure source wavelength.

Positive i-line resists typically consist of three components: a novolak resin; a photoactive compound (PAC), which is commonly a naphthoquinone diazide ester; and a solvent. Occasionally, a dye or other additive is added to improve the latitude of the lithographic process. DUV resists usually consist of three components as well. However, DUV resists contain a photo acid generator (PAG) rather than a PAC, which is often embedded within the high-molecular-weight polymer matrix.[1-2] In other formulations, the PAG is simply one of many components in the photoresist mixture. The photoresist used for our study is of the latter type. These resists must be thermally stable in order to withstand high-temperature environments such as plasma etching and ion implantation. They must also possess good adhesion properties 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 Beer's law of absorption can be used to calculate the change in light intensity within the photoresist.[3-5] Because of the complex nature of positive resists, both absorption and scattering must be considered when evaluating their optical properties. DUV light is routinely employed in the photolithographic process; it is expected that the photoresist will strongly absorb the UV light, while absorption of the longer visible light is negligible. This is an important consideration because visible light from a HeNe laser is used for target recognition and stepper alignment of wafers.

In this paper, we present an in-depth characterization of optical properties of a positive DUV photoresist. The optical properties investigated include index of refraction, absorption and scattering coefficients, total attenuation coefficient, and scattering anisotropy factor. We also compare these results with those obtained on g-line and i-line resists.[6-7] The information on 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:[8]

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

Equation 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 is the gain in *I(r,s)* per unit length in the direction *s* due to scattering from other scattered light *I(r,s')dΩ'* (i.e., light intensity confined in the elemental solid angle *dΩ'*) from direction *s'*. Even though the exact form of the phase function *p(s,s')* in turbid media is not known, Henyey-Greenstein phase function provides a good approximation for most practical purposes.[6] The Henyey-Greenstein phase function depends only on the scattering anisotropy factor *g*, which ranges from -1 for complete backward scattering to zero for absolute isotropic scattering to 1 for complete forward scattering.

Although the radiative transport theory gives a more adequate description of the distribution of photon intensity in the turbid medium than any other model, the general analytical solution is not yet known. 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. Nevertheless, knowledge of absorption and scattering coefficients of the turbid media, and scattering phase function, is needed to solve Equation 1 .

In recent years, the computational method known as inverse adding doubling (IAD)[9] has been employed along with Monte Carlo simulation techniques[10-12] to successfully determine such fundamental optical properties as absorption and scattering coefficients and scattering anisotropy factors of turbid samples. These methods provide by far the most accurate estimates of optical properties than any other models. Two dimensionless quantities used in the entire process of IAD are albedo α and optical depth τ, which are defined as:

$\alpha = \mu_s/(\mu_s + \mu_a)$ and $\tau = t(\mu_s + \mu_a)$

Equation 2

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

The measured values of the total diffuse reflectance and total diffuse transmittance, using an integrating sphere, and unscattered collimated transmittance, are applied to the IAD method to determine the optical properties of the photoresist samples. Employing this method, the optical properties are obtained by repeatedly solving the radiative transport Equation 1 until the solution matches the measured values.

Materials and methods

The positive DUV photoresist used in this study was the Arch 8250-10 from Arch Chemicals Inc. (Norwalk, Conn.). It consists of 1-Methoxy-2-propanol acetate (the solvent commonly known as PGMEA), derivatized polystyrene resin, triaryl sulfonium sulfonate (PAG), and 2-Methoxy-1-propanol acetate. According to the material safety data sheet supplied by Arch Chemicals, the percentage range of the 1-Methoxy-2-propanol acetate is 75-85%, the percentage range of the derivatized polystyrene resin is 15-25%, and the percentage range of the 2-Methoxy-1-propanol acetate is0.1-<0.5%. The latter component is an impurity of 1-Methoxy-2-propanol acetate. Information on the PAG is not mentioned in the data sheet. 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 0.1 cm.

Measurement of absorption spectra

The room-temperature absorption spectrum of the positive DUV photoresist sample was measured as 250-650 nm using a Hewlett-Packard Model G1103A UV-VIS spectrophotometer. Before taking the absorption spectrum on this sample, a base line 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 base line from the measured data.

Measurement of index of refraction

The index of refraction of the positive DUV photoresist was measured at four different wavelengths by the method of minimum deviation using a hollow quartz prism.[6] The 60° hollow prism was made of 1 × 2 cm quartz s lides obtained from NSG Precision Cell Inc. (Farmingdale, N.Y.). In this procedure, the hollow prism was firmly mounted at the center of a goniometer table. This method was chosen for its simplicity and accuracy.

Measurement of scattering anisotropy factor

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 (θ) using a goniometer table. The scattering anisotropy factor g is given by the average cosine of the scattering angle θ

according to the following expression:

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

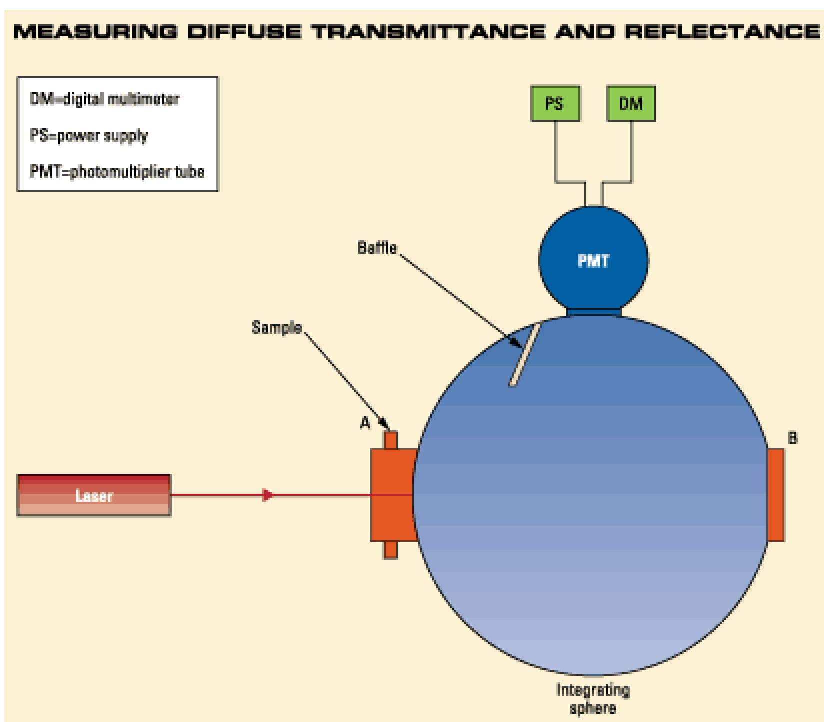
Equation 3

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. The scattering anisotropy factor g was measured and found to be 0.99. The experimental details for the measurement of g can be found in Reference 6 .

Measurement of total diffuse reflectance and total diffuse transmittance

The total diffuse reflectance and total diffuse transmittance measurements were taken using a single integrating sphere (Oriel Model 71400). The photoresist sample was placed in a specially designed holder, which mounted to one of the ports of the integrating sphere. The light source used for these measurements was a HeNe laser (Model 125A from Spectra Physics). The average output power of the laser was 50 mW, the beam diameter at $1/e^2$ was 2 mm, and the beam divergence was 0.70 mrad at 632.8 nm.

The schematic of the experimental setup employed to measure the total diffuse reflectance and total diffuse transmittance is shown in Figure 1 . The laser was directed into the entrance port A of the integrating sphere, whose exit port B is either open or capped with a reflective surface identical to that of the interior surface of the integrating sphere or the sample depending on the measurement taken. The diameter of the sphere was 6 in., and each port had a diameter of 1 in. Light leaving the sample was reflected multiple times off the inner surfaces of the sphere. A reflecting baffle within the sphere shielded the photomultiplier tube (PMT) 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 a PMT (Oriel Model 7068) attached to the measuring port. The PMT was powered by a high-voltage power supply (Bertan, Model 215). The signal from the PMT was sent to a digital multimeter (Emco, DMR-2322).



1. The experimental setup used to measure the total diffuse

transmittance (T_d) and total diffuse reflectance (R_d) used an integrating sphere. The laser was directed into the entrance port A of the integrating sphere, whose exit port is either open or capped with a reflective surface identical to that of the interior surface of the integrating sphere or the sample depending on the measurement taken.[6]

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:

$$R_d = \frac{X_r - Y}{Z - Y}$$

Equation 4

and

$$T_d = \frac{X_t - Y}{Z - Y}$$

Equation 5

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 nor a reflective surface at B.

Measurement of collimated transmittance

The unscattered collimated transmittance T_c was measured to determine the total attenuation coefficient. The collimated laser beam intensity was measured by placing the integrating sphere about 3 m from the sample so that the photons scattered off the sample would be prevented from entering the small aperture (about 3 mm in diameter) at the entrance port A. The sample was placed at 90° with respect to the incident laser beam . The collimated transmittance T_c was calculated by the relation:

$$T_c = \frac{X_c}{Z_c}$$

Equation 6

where X_c is the collimated light intensity and Z_c is the incident light intensity. From Beer's Law, the total attenuation coefficient can be determined from the following expression:

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

Equation 7

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

Inverse adding doubling

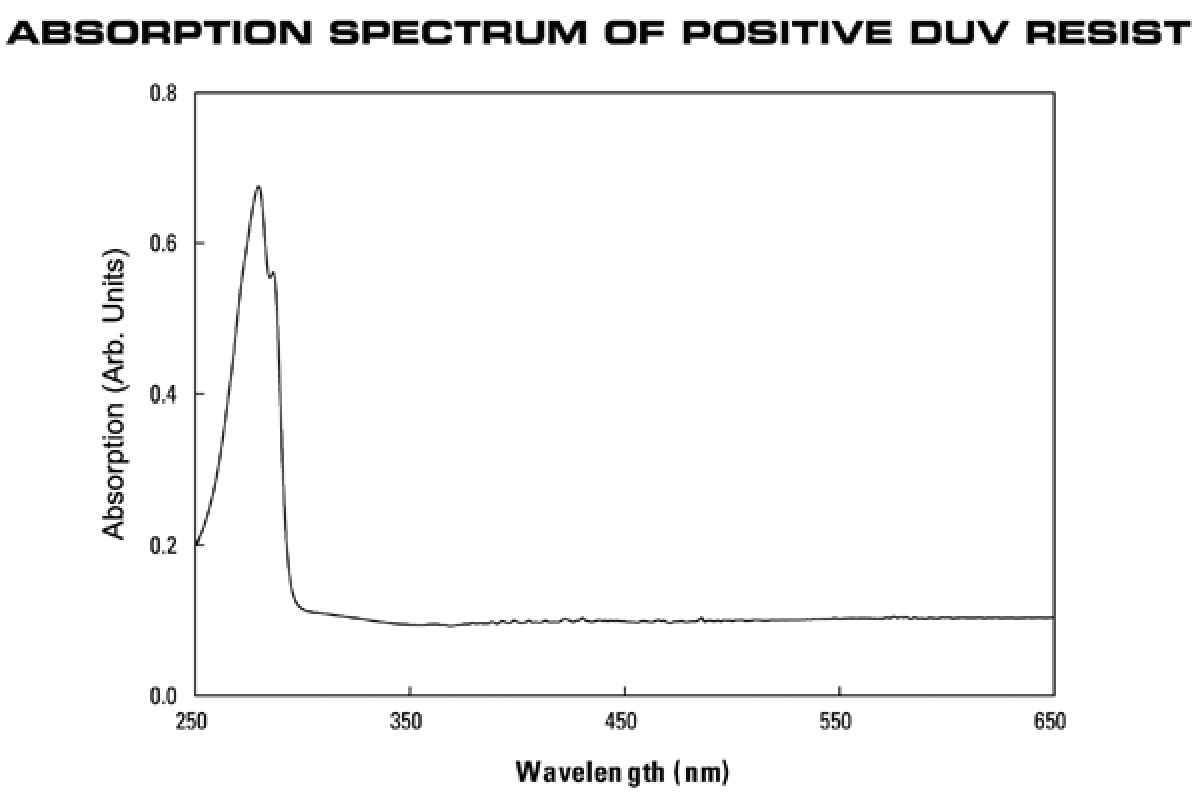
We have used the IAD method, which was originally developed by Scott Prahl of the Oregon Medical Laser Research Center,[9] to determine the optical properties of biological materials. To solve the radiative transport equation, the experimentally determined values of R_d, T_d, and g are imported to the IAD algorithm. The IAD algorithm iteratively chooses values for the dimensionless quantities, α and τ defined in Equation 2 , then adjusts the value of g until it generates values that match with the experimental values of R_d and T_d. The computed values for α and τ are then used to calculate the absorption and scattering coefficients.

Monte Carlo simulation

The accuracy of our measurements of R_d and T_d, used in the IAD method to determine the absorption and scattering coefficients, was verified by the Monte Carlo (MC) simulation technique. The MC simulation uses a 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 per wavelength 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. A detailed theoretical description of the MC model in biological media is given in Jacques et al.[12]

Results and discussion

The room-temperature absorption spectrum taken on the positive DUV photoresist sample between 250 and 650 nm on the HP UV-VIS spectrophotometer is shown in Figure 2 . The spectrum clearly shows that the absorbance of the photoresist sample is extremely high below 300 nm into the UV region, while it is significantly small above 300 nm. Using Beer's exponential decay law, the absorption coefficient at 632.8 nm was determined to be 0.1382 cm^{-1}. This value is somewhat less than the total attenuation coefficient of 0.525 cm^{-1} obtained from the measurement of the collimated transmittance T_c (Eq. 6). The larger absorption coefficient based on T_c is mainly due to 4% reflection losses off each of two glass interfaces used in the experimental setup. It should be noted that the total attenuation coefficient of 0.343 cm^{-1} obtained from the IAD method lies between the coefficients obtained from Beer's Law calculations and T_c.



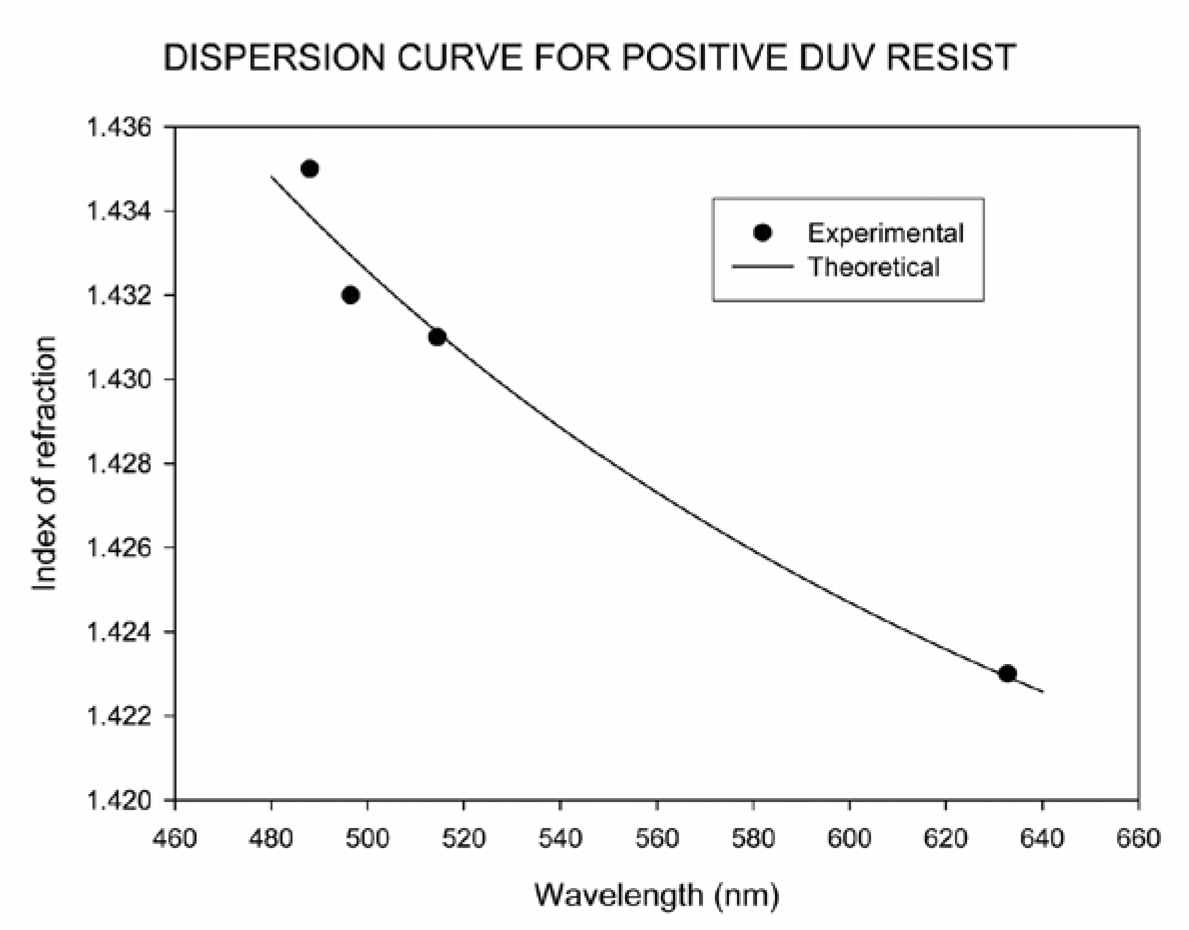
2. This chart shows the room-temperature absorption spectrum taken on the positive DUV resist sample between 250 and 650 nm.

The index of refraction of the positive DUV photoresist sample was measured at 488, 496.5, 514.5 and 632.8 nm, and the dispersion curve is given in Figure 3 . These measurements were repeated three times, and the values of index of refraction agreed to within 2%. The refractive index at 632.8 nm was determined to be 1.423, and this value was used in all subsequent calculations. The experimental data were subsequently fitted (shown in solid line) using the least-squares fitting program to the Sellmeier's dispersion equation:[13]

$$n^2(\lambda) = 1 + \frac{S\lambda^2}{\lambda^2 - \lambda_0^2}$$

Equation 8

The least-squares fit of the experimental data to the Sellmeier's equation provided the values of the constants, S=0.982 and λ_0=129.2 nm.



3. Experimental data of the dispersion curve for positive DUV resist were fitted using the least-squares fitting program to the Sellmeier's dispersion equation (Eq. 8).

The total diffuse reflectance and total diffuse transmittance were measured on a positive DUV photoresist sample using a 632.8 nm light source. These measurements were repeated three times, and the data were in excellent agreement. These values are given in Table 1 .

Table 1. R_d and T_d for Positive DUV Photoresist at 632.8 nm (g=0.99)			
Experimental		Monte Carlo	
R_d	T_d	R_d	T_d
0.0019	0.9223	0.0014	0.9108

For comparison, values from the previous g-line and i-line photoresist studies are shown in Tables 2 and 3 , respectively.

Table 2. R_d and T_d for Positive g-line Photoresist at 632.8 nm (g=0.95)			
Experimental		Monte Carlo	
R_d	T_d	R_d	T_d
0.003	0.726	0.001	0.797

Table 3. R_d and T_d 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 R_d and T_d, along with the measured value of the index of refraction of photoresist, 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 4 .

Table 4. R_d, T_d, T_c, α, τ, μ_a, μ_s, μ_t for Positive DUV Photoresist at 632.8 nm							
Experimental			IAD				
R_d	T_d	T_c	α	τ	μ_a	μ_s	μ_t
0.0019	0.9223	0.869	0.775	0.034	0.077	0.266	0.343

Results from the previous positive g-line and i-line experiments are listed in Tables 5 and 6 , respectively.

Table 5. R_d, T_d, T_c, α, τ, μ_a, μ_s, μ_t for Positive g-line Photoresist at 632.8 nm							
Experimental			IAD				
R_d	T_d	T_c	α	τ	μ_a	μ_s	μ_t
0.003	0.726	0.636	0.225	0.287	1.20	0.350	1.55

Table 6. R_d, T_d, T_c, α, τ, μ_a, μ_s, μ_t for Positive i-line Photoresist at 632.8 nm							
Experimental			IAD				
R_d	T_d	T_c	α	τ	μ_a	μ_s	μ_t
0.068	0.767	0.124	0.906	1.97	1.03	9.87	10.90

Because of the complex nature of positive photoresist, the scattering coefficient for the resist used in this study was found to be considerably higher than its absorption coefficient. However, the total attenuation coefficient for the positive DUV photoresist was ~5-32× smaller than that obtained in the previous research on g-line and i-line photoresists. The scattering anisotropy factor was determined to be ~0.99, indicating 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:[14]

$$D = c/3\left(\mu_s' + \mu_a\right)$$

Equation 9

where *c* is the speed of light in vacuum and μ'_s is the reduced (transport) scattering coefficient defined by $\mu'_s=(1-g)\mu_s$, which is calculated to be 0.003 cm^{-1}. The value of the photon diffusion coefficient is 1.26×10^{11} 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 12.55 cm.

The measured values of the total diffuse reflectance and total diffuse transmittance have been verified by the Monte Carlo simulation technique. The experimental and MC values for the total diffuse reflectance differed by ~26%, while the values for the total diffuse transmittance varied by <2%. The large discrepancy in R_d values 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.

The values of the optical properties of the positive DUV photoresist reported in this article are of significant importance to the semiconductor industry. A thorough knowledge of optical properties of photoresist is imperative for photoresist manufacturers and process engineers to be able to assess 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 due to the fact that most steppers in IC fabrication facilities use a HeNe laser light source for target recognition and alignment of semiconductor wafers.

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