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Absorbance measurement of polymers at extreme ultraviolet wavelength: Correlation between experimental and theoretical calculations

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Performance requirements for extreme UV (EUV) resists will require the development of polymer platforms. A challenge in designing photoresists for EUV wavelengths is the selection of molecular structures that have minimal absorbance. For example, elements that are commonly used in photoresists at other wavelengths, such as oxygen and fluorine, are highly absorbing at ~ 13 nm making them problematic for EUV applications. In order to provide a tool for EUV resist design, this article presents a study of the absorbance of common photoresist structures and compares it to theoretical estimates of resist absorbance based on composition and density. On this basis, several potential structures suitable for EUV resists are assessed. © 2006 American Vacuum Society.

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I. INTRODUCTION

In photolithography, feature size is ultimately limited by the wavelength of the exposing radiation. To accommodate the requirement of ever-decreasing integrated circuit (IC) size and increasing circuit density, extreme ultraviolet (EUV) radiation at a wavelength of 13.5 nm is being explored as the basis of next generation lithography to produce feature sizes under 32 nm. When designing resists for EUV technology, the primary concern is the absorption of light by the resist platform because most materials are highly absorbing. This concern is also magnified in the EUV node because of the lower power of exposure tools compared to current generation lithography tools. But can one quantify the absorption of a polymer resist, when so few EUV tools are available for direct measurement? And more importantly, how accurate are these approximations compared to “real” measurements?

At such wavelengths, absorption is dependent on atomic structure instead of chemical environment as found in current resist technology. To complicate the resist design, oxygen and fluorine are among the highest absorption elements, which preclude the use of many current strategies for high resolution chemically amplified resists. Figure 1 shows the atomic photoabsorption cross section of the elements ($Z = 1-50$).

As noted, absorbance of materials in the EUV (soft x-ray) region has different characteristics than that of previous generation of resists. Since photons in this spectral region have very high energy, it does not activate electrons in the valence shell, which are involved normally in chemical bonding, and

instead stimulates core shell electrons. As a result, absorbance of photoresist materials in this region is not affected by bonding characteristics as much as in the 157 or 193 nm regions. Furthermore, strong absorption in the soft x-ray region by most elements makes the choice of elements for constructing resists extremely narrow.

Theoretically, the photoabsorption of materials in the soft x-ray regions can be calculated by using known atomic scattering factors $f = f_1 + if_2$ as long as the energy of the photon is outside of the absorption threshold regions. The atomic photoabsorption cross section μ_a may be readily obtained from the tabulated values of f_2 using the relation,

$$\mu_a = 2 \times r_0 \times \lambda \times f_2, \quad (1)$$

where r_0 is the classical electron radius, λ is the x-ray wavelength, and f_2 is the imaginary part of atomic scattering factor. Using the atomic photoabsorption cross section, the lin-

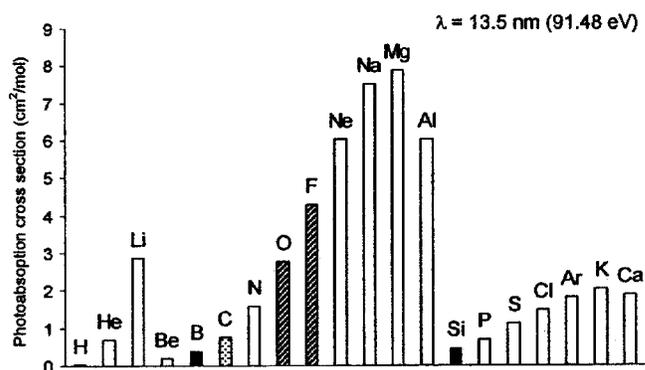
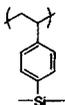
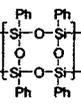
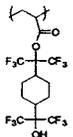


FIG. 1. Photoabsorption cross section of first and second row elements at 13.5 nm.

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TABLE I. Selected polymer platforms, structure, and chemical characteristics.

Name	Structure	Preparation	M_n	PDI
poly(methyl methacrylate) (PMMA)		Aldrich	18100	1.68
polynorbornene (PNB)		[Pd]	not determined	
polystyrene (PSt)		Aldrich	13700	1.05
poly(hydroxystyrene) (PHOSt)		AIBN	3600	1.46
poly(trimethylsilyl styrene) (PTMSSt)		AIBN	13000	1.68
poly(methylphenyl silane) (PMPS)		Gelest	11100	2.56
poly(phenylsilsesquiazane) (PPSSQ)		Gelest	860	2.38
157 nm resist (PAF)		AIBN	1500	6.66

ear absorption coefficient (μ) of a specific material can be calculated by

$$\mu = \frac{N_A \rho}{MW} \sum_i x_i \sigma_{ai},$$

$$MW = \sum_i x_i A_i, \quad (2)$$

where ρ is the density, x_i is the number fraction of element i , and A_i is the atomic weight of element i . In this way, as long as the density of the material is known, the absorption at EUV wavelengths can be calculated.¹ This approach may be extremely useful in the design of transparent resist platforms for EUV lithography.

In this article, we present a systematic study of the correlation between the calculated and experimentally measured linear photoabsorption coefficient for a series of general resist platforms aiming to answer questions currently in the resist community about what are superior resist materials when designing new resist platforms for EUVL. Our findings are discussed with emphasis on elemental resist composition as models for backbone structures and materials film properties such as density.

II. EXPERIMENT

Materials including metal complexes were obtained from commercial suppliers and used without further purification

unless otherwise noted. Tetrahydrofuran (THF) was purified as moisture free by distillation from sodium and benzophenone. The fluorine-containing polymer (PAF), polymethylphenylsilane, and polynorbornene were synthesized in-house following published procedures.²

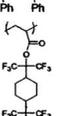
Density calculation. The density was determined using the “weight” method. Resists were spun uniformly on a previously weighed Si wafer. The thickness of the resist is measured and the mass of the resist alone is calculated by subtracting the measured weight of the resist on Si with that of the Si wafer. The density was obtained using the following formula for density as mass per unit volume:

$$\text{Density} = \frac{\text{Mass}_{\text{resist on wafer}} - \text{Mass}_{\text{wafer}}}{\pi r^2 \times \text{resist thickness}}. \quad (3)$$

In our experiment, a silicon wafer was weighed before and after spin coating the polymer and the thickness of the film determined using a Tencor P10 profilometer. The procedure was repeated for each polymer.

Experimental absorbance measurements. The measurement of absorbance was performed at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, using the grazing incidence angle method. In this method, the reflectivity at 13.5 nm of a polymer coated onto a silicon wafer was measured as a function of the angle.

TABLE II. Measured density and calculated absorption coefficients for resists platforms.

Name	Structure	Formula	Density (g/cm ³)	Calculated Linear absorption coefficient (μm ⁻¹)
PMMA		C ₅ H ₈ O ₂	1.18	5.19
PNB		C ₇ H ₁₀	0.92	2.55
PSt		C ₈ H ₈	1.05	2.95
PHOSt		C ₈ H ₈ O	1.16	4.05
PTMSSSt		C ₁₁ H ₁₆ Si	1.14	2.78
PMPS		C ₇ H ₈ Si	1.12	2.60
PPSSQ		C ₂₄ H ₂₀ Si ₄ O ₄	1.50	4.52
PAF		C ₁₅ H ₁₄ O ₃ F ₁₂	1 ^a	6.97

^aDensity could not be determined so an approximated value of 1 was used.

III. RESULTS AND DISCUSSION

Based on the photoabsorption cross-section data for the elements, carbon, hydrogen, and silicon are especially interesting elements because of their low values at 13.5 nm (Fig. 1). Using these elements as building blocks for next generation resists might be advantageous. But questions remain about whether elements such as silicon are viable for this particular wavelength?

Theoretically, the atomic scattering factors are based upon photoabsorption measurements of elements in their elemental state. A fundamental assumption is that the condensed matter may be modeled as a collection of noninteracting atoms. This assumption is, in general, a good one for energies sufficiently far from absorption thresholds. In the threshold regions, the specific chemical state is important and direct experimental measurements must be made. Si has its absorption threshold at ~100 eV (~12.3 nm) (Ref. 3) which is close to the target wavelength of 13.5 nm. Therefore it is important to directly measure the absorbance of real polymers to determine how absorbance correlates with theoretical calculations. At the same time, oxygen is a strongly absorbing element that is key to chemically amplified systems. The homopolymers selected for this study were chosen to cover both a wide range of absorbance values and they are commonly used backbone structures in resist technology. In this way, a good general backbone polymer could be selected for

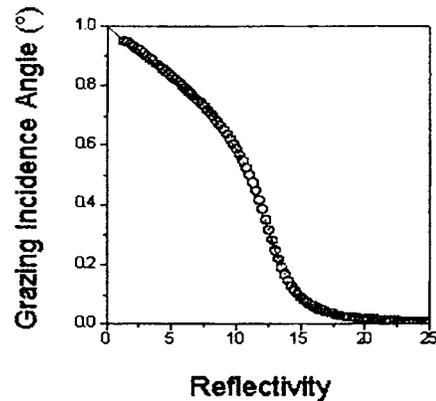


FIG. 2. Reflectivity vs angle for the measurement of PMMA.

the design of next generation resists. Table I shows the selected platforms and the properties of the homopolymers.

Density was determined by measuring resist mass on six wafers before and after coating and calculating volume based on surface area and thickness. When available, the value of determined density was compared to a published value.⁴ Experimental values were typically $\pm 5\%$ of reported values of density and thus may overestimate the calculated absorbances. These results are, however, consistent with previous investigations of density calculations by the "weight" method and specular x-ray reflection (SXR) measurements,⁵ despite the known error in density determination using the "weight" method. The values of calculated densities are shown in Table II.

The calculated absorption coefficient for the selected polymer platforms was determined using the density and chemical composition data using computational tools available at the Centre for X-ray Optics and Advanced Light Source website. When undetermined, as in the case of PAF in Table II, an estimated density value of 1 was used.

The measurement of absorbance was made using the grazing incidence angle method. In this approach, polymer samples were deposited onto silicon wafers and the grazing incidence reflectivity at 13.5 nm was measured as a function of angle. For example, the data for the PMMA grazing angle experiment is shown in Fig. 2.

This behavior is described by the Fresnel equation for reflectivity,

$$R_S = \left| \frac{\sin \theta - \sqrt{n^2 + \cos^2 \theta}}{\sin \theta + \sqrt{n^2 + \cos^2 \theta}} \right|^2 \quad \text{with } n = 1 - \delta + i\beta, \quad (4)$$

where R_S is the reflectivity of the film, θ is the angle of reflection, and n is the refractive index of the polymer film. The imaginary part β (extinction coefficient) of the refractive index can be obtained by fitting the experimental data using a linear least-squares method. In the case of poly(methyl methacrylate) (PMMA), the best fit data gives the values for δ and β as 0.0242 and 0.0054, respectively. The resulting values of δ and β satisfy the condition $\delta > \beta$ that is needed to validate the grazing incidence measurements.⁵ From these

TABLE III. Calculated and measured absorbances for investigated polymer platforms.

Name	Density (g/cm ³)	Calculated A (μm ⁻¹)	Measured A (μm ⁻¹)	D %
PMMA	1.18	5.19	5.03	3.1
PNB	0.92	2.55	2.58	-1.2
PSt	1.05	2.95	2.70	8.5
PHOS _t	1.16	4.05	3.88	4.2
PTMSS _t	1.01	2.47	2.14	13.4
PMPS	1.12	2.60	2.82	-8.5
PPSSQ	1.50	4.52	4.45	1.5
PAF	1	6.97	10.75	-54.2

values, the absorbance of the polymer film can be calculated by using Eq. (5).⁶

$$A = \mu = \frac{4\pi}{\lambda} * \beta, \quad (5)$$

where μ is the linear absorption coefficient and λ is the irradiation wavelength. For PMMA, the experimental absorption coefficient corresponds to 5.03 μm⁻¹. In a similar manner the reflectivity versus angle and linear absorption coefficients for all samples were measured and calculated. The results are presented in Table III together with the calculated values. The experimental values correspond well with the theoretical calculations for the polymers when the density has been previously measured (Fig. 3).

Table III also shows that the silicon containing polymers are the more transparent polymers. Experimentally measured absorbance strongly supports the thesis that incorporation of silicon improves transparency. Again we want to emphasize that incorporation of silicon alone is not enough and density must be considered into the final analysis. It appears that decreasing the density of the final polymer is an important variable that has to be addressed when designing polymers for extreme ultraviolet lithography (EUVL).

When comparing poly(trimethylsilylstyrene) (PTMSS) and poly(methylphenylsilane) (PMPS), even though there is a higher silicon content in PMPS, the latter is less transparent than PTMSS. We believe that this difference is a direct consequence of the higher density shown by PMPS. However, it is also possible, because of the method of synthesis of PMPS (Wurtz condensation), that some oxidation of the polymer chain may occur thus resulting in a higher absorbance compared with oxygen free PMPS. Experimentally, PMPS shows a higher value of absorbance compared to the theoretical value based on chemical composition. Polyphenylsilsesquioxane (PPSSQ), one of the most widely used silicon-containing polymers for a photoresist, shows high absorbance even though it has high silicon content. This is a consequence of its high oxygen content, offsetting the positive effect of silicon making these types of polymers much less desirable for EUVL.

Polymers with high H/C ratios such as polynorbornene (PN) did show good transparency, indicating that a good polymer backbone for resist platforms could be based on

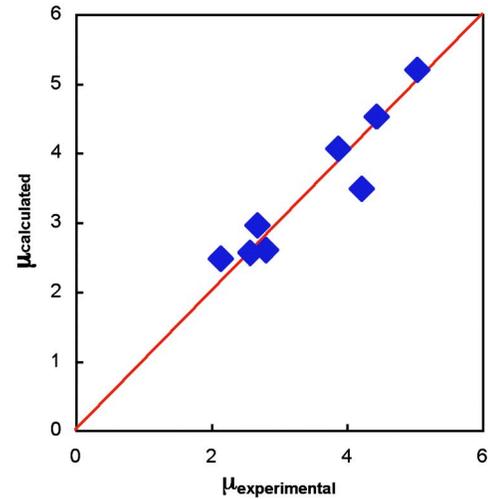


FIG. 3. Calculated and experimental linear absorption coefficients.

norbornene-type polymers. Incorporation of silicon (for example, trimethylsilane), could significantly improve transparency, assuming no change in density, improving it from 2.58 to 2.17 μm⁻¹.

For PAF, the discrepancy observed between calculated and measured absorbances is attributed to using an estimated density value of 1.0. When the density of PAF was calculated from its experimental absorbance value, it clearly shows the influence that the density has in the final determination of absorbance. Using the experimental absorption of the polymers, a calculated density was obtained for all the polymers (Table IV). The calculated values of density are in reasonable agreement with experimental values, thus supporting the utility of this method.

IV. CONCLUSION

The absorbance of various polymers in the EUV region (13.5 nm) was determined using the grazing incident angle method. The measured absorbance values match very well with theoretical estimates based on tabulated values of photoabsorption cross-sections. A reliable measurement of the

TABLE IV. Calculated and measured density for the polymer platforms.

Name	Measured density (g/cm ²) ^a	Calculated density (g/cm ²) ^b
PMMA	1.18	1.14
PNB	0.92	0.94
PSt	1.05	0.96
PHOS _t	1.16	1.14
PTMSS _t	1.01	0.88
PMPS	1.12	1.13
PPSSQ	1.50	1.48
PAF	...	1.54

^aFrom "weight" method.

^bFrom absorbance experiments.

density is required to obtain meaningful absorbance values. These studies indicate that the increased silicon content does reduce overall absorbance at EUV wavelength, provided more oxygen is not added at the same time. Resist density may also be considered as a tool for increasing overall transparency. This study demonstrates that information about EUV resist absorbance may also be reliably obtained even for hypothetical polymers knowing only atomic composition and a reasonable estimate of density.

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³Data from the Center for X-Ray Optics (CXRO) at Berkeley National Laboratory website at <http://xdb.lbl.gov/>

⁴PMMA and polystyrene were purchased from Aldrich.

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