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H. R. Philipp, H. S. Cole, Y. S. Liu, and T. A. Sitnik

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H. R. Philipp, H. S. Cole, Y. S. Liu, and T. A. Sitnik

General Electric Corporate Research and Development, Schenectady, New York 12301

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Absorption coefficients for some technologically important polymer materials are given in the wavelength range ~240–170 nm. Absorption coefficients at 193 nm for these polymers show a wide range of values from ~2×10^2 cm^−1 for polytetrafluoroethylene (Teflon) to ~4×10^4 cm^−1 for polyimide. The general nature of the optical properties of polymers in the vacuum ultraviolet is also discussed.

Polymers comprise a class of technologically important materials and there is presently much to be learned concerning their electronic properties. Some of this information is obtained through optical studies in the region of strong fundamental absorption. While the optical properties of most polymers are reasonably well known for wavelengths above 200 nm, in the vacuum ultraviolet, \( \lambda < 200 \) nm, where the principle absorption bands of these materials often lie, this information is generally lacking. To our knowledge, few, if any, studies have been undertaken to evaluate the optical properties of polymers in the vacuum ultraviolet spectral region. Recently, additional interest has developed in the process of photodissolving of polymeric materials by ultraviolet laser irradiation especially at the ArF excimer laser wavelength of 193 nm. Both photochemical and photothermal mechanisms have been proposed to explain the dry etching phenomena of such materials. An important and indeed essential parameter in the description of the laser polymer interaction is the optical absorption coefficient of the material being irradiated. We report here absorption data for a variety of polymers in the region 240–170 nm which includes the ArF excimer laser wavelength at 193 nm. A 1-m, normal incidence, concave grating vacuum monochromator was used for these measurements. A general discussion is also given of the expected behavior of the real and imaginary parts of the complex index of refraction of polymers in the vacuum ultraviolet.

In this letter the absorption of light is described by the absorption coefficient \( \alpha \), which is determined from transmission measurements using

\[ I = I_0 e^{-\alpha x}, \]

where \( I \) and \( I_0 \) are transmitted and incident intensity, respectively, and \( x \) is the sample thickness. Except where indicated, the polymers were dissolved in a suitable solvent and spin coated on quartz substrates. These samples were vacuum baked prior to measurement to remove the solvent and trace amounts of moisture. All polymers used were additive free except the commercial sheet materials which may contain small amounts of proprietary additives. It is conceivable that such additives could contribute to the optical absorption of the sheet materials. The incident intensity \( I_0 \) was corrected for absorption due to the substrate and for sample-substrate reflectance losses. Thicknesses of polymer samples on quartz were measured using a Sloan Dektak II. This instrument is an automated surface profiler capable of accurately measur-
the entire spectral range of measurement. For polyimide, the results are in reasonably good agreement with those measured by Ishida et al. and reported by Karen and Yeh for excimer laser wavelengths at 193, 248, and 351 nm.

In Fig. 4, absorption data are given for the polymers poly (tetrafluoroethylene) [PTFE], polyethylene [PE], polypropylene [PP], and nitrocellulose, for the copolymer styrene allyl alcohol [SAA] and for the polymer-monomer mixture PVA plus 25 wt % biphenyl carbonitrile. The data for PTFE (trade name: Teflon resin), PE, and PP were obtained on commercial sheets. These data show a large range of absorption coefficient obtainable in polymer films and point out several ways in which the absorption in a given polymer can be altered by either the addition of an absorbing monomer or by forming copolymers with polymers of different absorption. We have examined photoetching properties at the ArF excimer laser wavelength of 193 nm in a polystyrene-PMMA copolymer system where the absorption was varied from \( \approx 2 \times 10^3 \) to \( \approx 8 \times 10^4 \) cm\(^{-1}\). These results will be published shortly. We also note that polymers such as PTFE are possible candidates for use as a pellicle material for mask protection in deep ultraviolet photolithography.

A further comment can be made concerning the expected general behavior of the real and imaginary parts of the complex index of refraction,

\[
N = n - ik
\]

for the polymer materials discussed here. The absorption structure in these polymers appears to be very broad with maximum values of absorption coefficient \( \alpha_{\text{max}} \lesssim 10^6 \) cm\(^{-1}\). Hence, in the vacuum ultraviolet we anticipate

\[
k_{\text{max}} = \frac{\lambda \alpha_{\text{max}}}{4\pi} \lesssim 1.
\]

The index of refraction \( n \) and the extinction coefficient \( k \) or absorption coefficient \( \alpha \) are, of course, not independent parameters but are connected by Kramers–Kronig relations which can be put in various forms. The one connecting \( n \) and \( \alpha \) can be written

\[
n(E_0) = 1 + \frac{\lambda(E_0)}{4\pi^2} \int_0^E \frac{d\alpha(E)}{dE} \ln \frac{E + E_0}{E - E_0} dE,
\]

where \( E \) is the photon energy, \( E = h\nu/\lambda \). If \( d\alpha/dE \) is small for energies \( E \) in the vacuum ultraviolet, then we can expect the energy or wavelength dependence of \( n \) to be relatively small. On this basis we anticipate that the maximum values of \( n \) for those polymers should not be appreciably greater.
than those observed at long wavelengths, say in the visible region of the spectrum. Hence for a polymer of nominal index 1.6 at visible wavelengths, we expect $n_{\text{max}} \sim 1.9-2.2$ and for this maximum value to occur at a wavelength near the peak of the first strong absorption band ($\alpha > 10^5 \text{ cm}^{-1}$). This further implies that the normal incidence reflectance

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

of these polymers in the vacuum ultraviolet should generally be low with $R_{\text{max}} \leq 0.2$. Studies, currently in progress, which extend the range of measurement to 105 nm and evaluate $R$, $n$, and $k$ are consistent with the above comments.

In summary, we emphasize that the results presented here at 193 nm are, in most cases, the only optical data presently available for use in describing the ArF laser interaction with such materials. The understanding of the photoetching process and its optimization have important implications in microelectronic fabrication.

14A trade name of E. I. DuPont De Nemours and Co., Wilmington, DE.
17See, for example, T. S. Moss, Optical Properties of Semiconductors (Butterworths, London, 1959), Chap. 2.