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Films of PMMA including azobenzene were prepared by casting polymer solutions containing the probe or by exposing pre-irradiated films to the vapor of azobenzene. Under similar conditions, films which had been irradiated imbibed more azobenzene than annealed, unirradiated films or irradiated films which had been annealed above T_g. These materials were irradiated at 335 nm and the amount of trans azobenzene which had been formed was monitored spectrophotometrically. The largest amount of photoisomerization was observed for the pre-irradiated samples which had been penetrated by azobenzene from the vapor, indicating that the created free volume allowed the isomerization to proceed more easily.

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DIRECT EVIDENCE FOR THE CREATION OF MICROPORES IN UV-IRRADIATED POLY(METHYL METHACRYLATE)

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ABSTRACT

Films of PMMA containing azobenzene were prepared by casting from polymer solutions containing the probe or by exposing pre-irradiated films to the vapor of azobenzene. These materials were irradiated at 335 nm and the amount of trans azobenzene which had been photoisomerized was monitored spectrophotometrically. The largest amount of photoisomerization was observed for the pre-irradiated samples which had been penetrated by azobenzene from the vapor, indicating that the created free volume allowed the isomerization to proceed more easily.

INTRODUCTION

When polymers are exposed to ultraviolet and high energy radiation, changes of chemical properties (scission or crosslinking) can be detected experimentally and should be associated with changes in the physical properties such as the local free volume [1-3] and glass transition temperature [4, 5]. These changes of chemical and physical properties affect the solubility characteristics in the irradiated area of polymer films and play a major role in lithographic materials [1-3].

Degradation of PMMA by various types of radiation such as ultraviolet, x-ray, γ-ray, electron and proton beams has been of interest both from the basic and practical point of view [6, 7]. Exposure of PMMA films to these radiation sources results in reduced molecular weight, the generation of unsaturated bonds by the scission of side chains, the evolution of gaseous products, and the appearance of the characteristic electron spin spectra of propagating [8] and peroxy radicals [9]. These chemical changes should be associated with the increase of local free volume (creation of micropores) in the irradiated PMMA.

A detailed study of the factors affecting the dissolution rate of PMMA film showed that the magnitude of the increase in the dissolution rate of irradiated film could not be entirely attributed to the reduction of the molecular weight [1, 2]. The evolution of gaseous products, i. e., CO, CO_2, HCO_2CH_3, CH_4, and CH_3OH, would cause an increase in local free volume in the irradiated film. Ouano observed indirect evidence of micropore formation in the irradiated PMMA from a study of changes in the dissolution rate (S) based on the solvent molecular weight (M_s) of a homologous series of n-alkyl acetate solvents. As the micropores become more numerous and larger with increasing radiation dose, the diffusion process of butyl acetate and the higher acetate homologs becomes less hindered, thus the break in the logS vs. logM_S becomes less pronounced. When PMMA films were prepared containing Meldrum's diazo as a dopant. the dopant acted as a mild retarder of film dissolution [10]. Upon irradiation at 254 nm. CO. N_2 and acetone as photoproducts diffused quickly out of the film leaving microvoids in the PMMA films. This process led to a pronounced acceleration of dissolution in the irradiated areas.

The presence of micropores in the polymer matrix permits increased diffusion compared to the homogenous polymer - penetrant system [11]. Therefore. the formation of micropores should affect the sorption of penetrants in the irradiated PMMA film. There are a variety of methods for measuring the sorption of a penetrant in polymers [11. 12]. However. these methods are not easily employed for the determination of sorption in a microthin film on a silicon wafer substrate. On the other hand. the sorption of a species. which has a very high extinction coefficient ($\approx 10^4$ l/mol-cm) compared to PMMA film. can penetrate PMMA film and the amount of a reporter molecule such as naphthalene absorbed in the irradiated PMMA films can be easily determined spectrophotometrically.

In recent reviews [13. 14]. the dominant factor in the photoisomerization of labels in polymeric solids is the local free volume in the vicinity of the label. because photoisomerization is strongly dependent on the rotational mobility of the label in the matrix. Analyses of the photoisomerization behavior of photochromic labels allows the study of processes such as physical aging. plasticization. and volume dilation caused by glassy deformation to be monitored sensitively. The free volume and the size distribution of free volumes in polymeric systems have been probed by the use of photochromic labels [15. 16]. In this work. azobenzene was used as a molecular label to study the formation of micropores in irradiated PMMA film. Trans azobenzene located in a PMMA matrix is photoisomerized when exposed to UV light of appropriate wavelength. The amount of photoisomerization (trans to cis) of azobenzene irradiated for a specific time was used to probe the formation of micropores in PMMA films by UV irradiation.

EXPERIMENTAL

Sorption of Naphthalene and Azobenzene in Irradiated PMMA Films

An irradiated PMMA film on a quartz disk was placed in a chamber containing napththalene or trans azobenzene crystals. which were used in commercial grade. The sample disks were positioned at about 5 cm from the bottom of the container to avoid contact between the crystals and the films. The closed container was stored in an oven at 50 ~ 60 °C to increase the rate of sublimation of naphthalene or azobenzene. Immediatetly after the sample was removed from the sorption chamber. its UV absorption spectrum was measured.

Photoisomerization (Trans to Cis) of Azobenzene in PMMA Films

PMMA films containing trans azobenzene were exposed to a flash UV light from a PRA flash lamp (Model 6199A) by using a narrow band interference filter (335 ± 10 nm). The UV spectra of samples changed photochemically were measured with a Perkin Elmer UV spectrophotometer immediately after a given number of flashes.

RESULTS AND DISCUSSINS

There are a variety of methods for measuring the sorption of a penetrant in polymer films. The most general procedures involve gravimetric and volumetric determinations. However, these methods are not easily employed for the determination of sorption in an ultra-thin film on a silicon wafer. On the other hand, sorption in PMMA films can be measured spectrophotometrically by using aromatic compounds as a probe. Naphthalene (solubility parameter, $\delta = 9.9\ [\mathrm{cal/cm^3}]^{1/2}$) was chosen as the sorption species because its vapor does not dissolve PMMA films at 60 °C and it is sublimed at a rate slow enough to be disregarded with respect to the loss of naphthalene during the spectroscopic measurement.

UV-irradiated and unexposed PMMA films were exposed to naphthalene vapor sublimed at 60 °C in the same vessel. The difference spectra of UV-irradiated PMMA films before and after naphthalene sorption are shown in Figure 1.

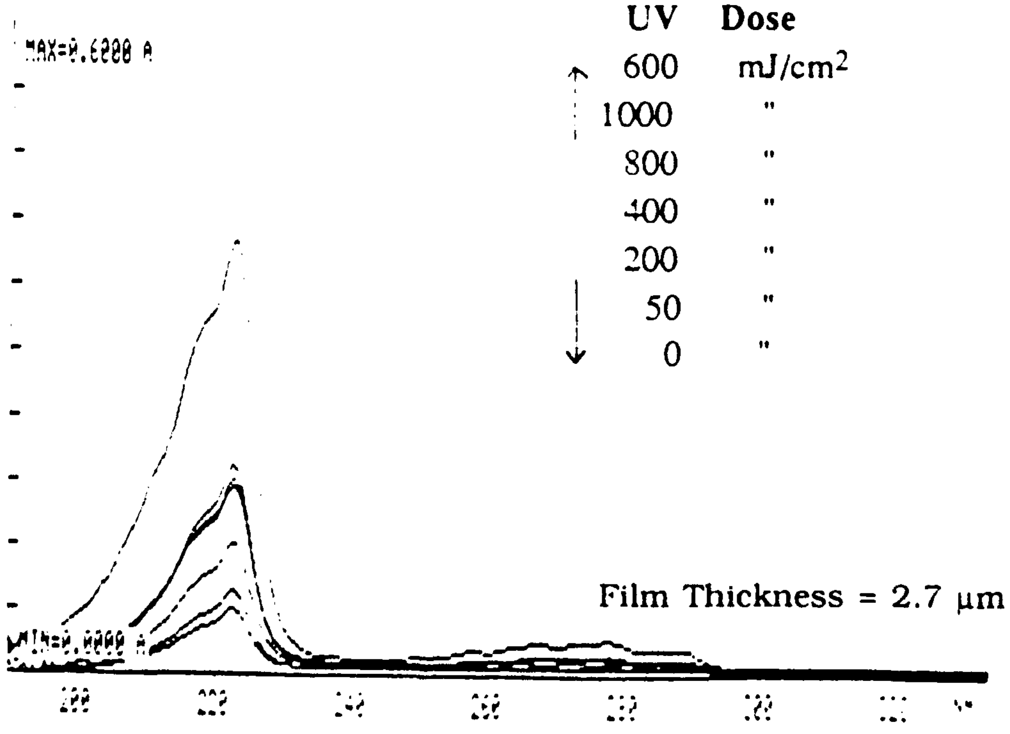

Figure 1. UV Difference Spectra of UV-Irradiated PMMA Films before and after Naphthalene Sorption at 60 °C for 3 Hours.

The amount of naphthalene imbibed by these samples was dependent on the incident dose. Under the same conditions, irradiated films imbibed more azobenzene than unirradiated films or irradiated films which had been annealed above T_g. PMMA films irradiated with electron and proton beams showed a similar trend of naphthalene sorption. The concentration of absorbed material was calculated from the UV difference spectra by using Beer's equation and is plotted in Figure 2. The absorbtion of naphthalene in PMMA films increases with longer exposure to radiation, then decreases beyond a certain dose. The azobenzene sorption in UV-irradiated PMMA films showed the same trend as naphthalene. These data indicate that the creation of micropores in PMMA film by radiation could be indirectly determined by the sorption. Further, the creation of the micropores may have been limited by recombination of polymeric fragments beyond a certain dose.

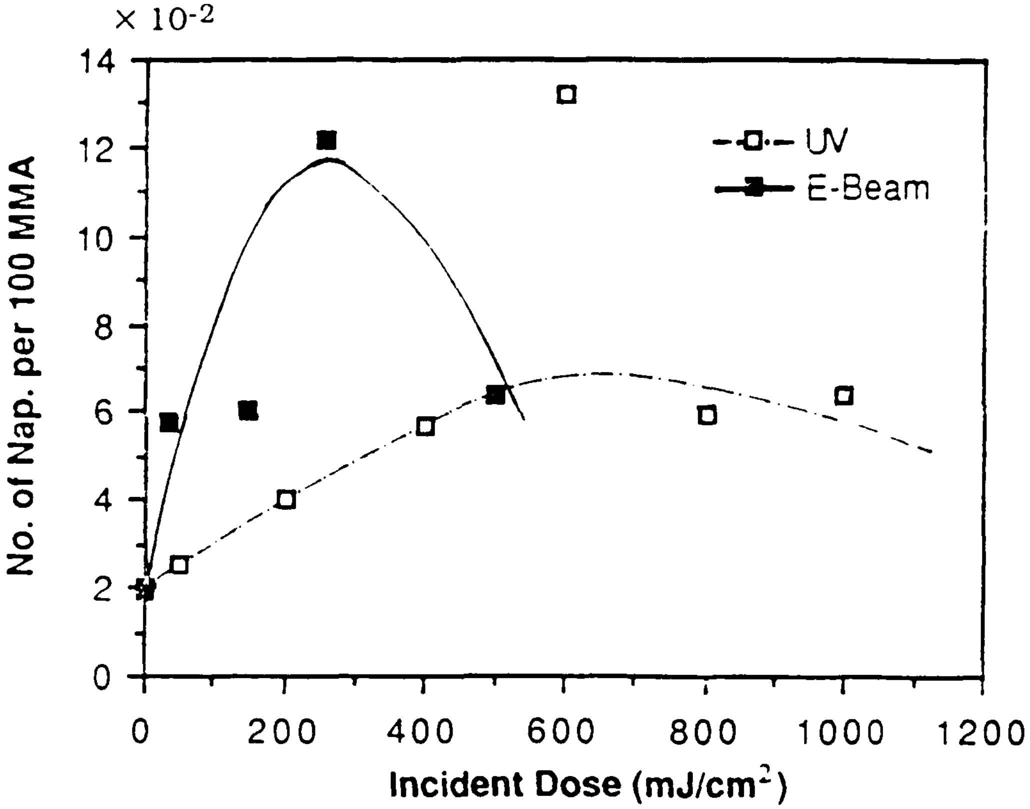

Figure 2. Plot of Naphthalene Sorption vs. Incident Dose in PMMA Film (≈ 3 μm) at 60°C for 3 Hours.

It was reported that the free volume in the polymer matrix could be probed by the use of photochromic labels [13-16]. Analysis of the photoisomerization behavior of photochromic labels within local free volume should be applicable to the study of the creation of micropores in a PMMA film irradiated with UV light. In this work, azobenzene was used to monitor the creation of micropores spectrophotometrically. Azobenzene exists as the extended trans isomer under normal conditions, but upon irradiation at 335 nm it is isomerized to the compact cis isomer by rotation about the weakened N=N bond in the excited state. Clearly this isomerization process will be affected by the amount of space (local free volume or microporosity) available on the molecular level as long as it is small compared to the molecular dimensions of the probe. The amounts of photoisomerization (trans to cis) were compared in the various samples prepared by different methods. Figure 3 shows changes in the UV spectra of azobenzene in PMMA film upon exposure to UV light at 335 nm.

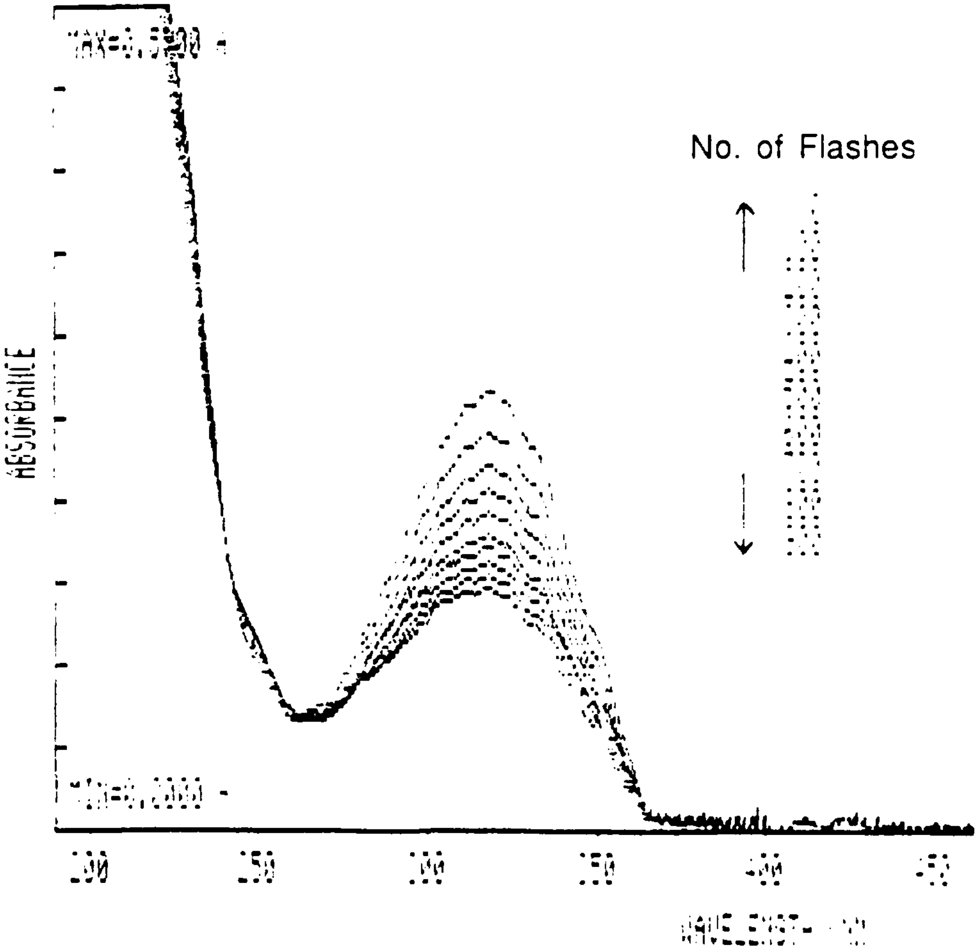

Figure 3. Changes of the UV Spectrum of Azobenzene in Irradiated PMMA Film by Exposure to UV Light (335±10 nm).

The amount of photoisomerization of azobenzene can be determined from the changes in the UV spectrum, assuming that the thermal and photochemical re-isomerization (cis to trans) is negligible in the early stages. Four PMMA samples, where azobenzene would be located in different amounts of free volume, were prepared as described below.

(A) Irradiated PMMA film was exposed to azobenzene vapor at 55 °C for 24 hours. Most of the azobenzene would enter micropores created by degradation of PMMA by UV light.

(B) A benzene solution of PMMA containing azobenzene was used for spin-coating. When the resulting thin film was baked at 130 °C for 30 minutes, only azobenzene remained in the PMMA film.

(C) Azobenzene was sorbed in PMMA film by exposing unirradiated films to azobenzene vapor at 120 °C.

(D) Irradiated PMMA film was exposed to azobenzene vapor at 55 °C and annealed at 120 °C in the presence of excess azobenzene to prevent its loss during the annealing process. The micropores should be collapsed and azobenzene would be contained in the original (before irradiation) free volume of PMMA film.

The concentration of azobenzene in PMMA was in the range of 0.3 ~ 1.3 molecules per 100 MMA repeating units. The extent of photoisomerization of azobenzene in Table I clearly shows the dependence on the method of sample preparation.

Table I. Photoisomerization of Azobenzene from Trans to Cis by 335±10 nm UV Light.

Samples		Photoisomerization (trans to cis)		Concentration of azobenzene per 100 repeating units
		100 flashes	200 flashes	
A	AZB diffused into irradiated PMMA film	12.9 %	30.0 %	0.5 AZB/100 MMA
		13.8 %	25.0 %	0.3 AZB/ "
B	AZB co-cast in PMMA film	7.4 %	10.8 %	0.6 AZB/ "
		8.4 %	15.3 %	1.3 AZB/ "
C	AZB diffused into PMMA film	7.5 %	13.7 %	1.1 AZB/ "
		7.5 %	15.2 %	0.5 AZB/ "
D	AZB diffused and annealed in irradiated PMMA film	9.9 %	13.2 %	0.6 AZB/ "
		9.3 %	18.2 %	0.5 AZB/ "

The largest amount of photoisomerization was observed for the pre-irradiated samples (A) which has been penetrated by azobenzene from the vapor, indicating the created free volume allowed the isomerization to proceed more easily. This result is direct evidence that a larger local free volume was created in PMMA films after UV-irradiation.

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