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Dopant-Induced Excimer Laser Ablation of Poly(tetrafluoroethylene)

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Abstract. Poly(tetrafluoroethylene) (PTFE) does not exhibit excimer laser etching behavior at conventional, e.g., single photon absorption, emissions of 193, 248, and 308 nm, due to the lack of polymer/photon interaction. This is not surprising since the electronic transitions available to the PTFE molecule are high energy and thus require short wavelength the radiation However, by incorporating a small quantity of material into the non-absorbing fluoropolymer matrix that interacts strongly with the emitted laser energy, e.g., a dopant, successful ablation, both in terms of etch rate and structuring quality occurs. Specifically, excimer laser ablation of PTFE films containing 5, 10, and 15% polyimide (wt/wt) as a dopant was achieved at 308 nm in a fluence range of 1 to 12 J/cm^2. Ablation rates for the materials increased with increasing fluence and, at the polyimide levels investigated, varied inversely with dopant concentration. All compositions exhibited excellent structuring quality.

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Since Kawamura et al. [1] and Srinivasan and Mayne-Banton's [2] initial findings using high-energy ultraviolet (UV) radiation to photoetch polymers, substantial research efforts have been undertaken to investigate the polymer structuring and processing phenomena utilizing excimer lasers [3–5]. The ability to ablate polymers by high-intensity UV exposure has resulted in tremendous excitement, especially in areas such as electronics and medicine. This excitement, in large part, is due to the technique's capability to cleanly and precisely remove small quantities, on the submicron level, of material from the polymer's exposed area in a uniform and controlled fashion.

Not all polymers are amenable to excimer laser structuring. For excimer ablation of a material to occur, the photons emitted by the laser must be absorbed. If a polymer's molecular structure does not contain the proper chemical functionality, i.e., chromophores, to provide the required absorption of the laser's photons, ablation will not occur. However, several investigators have reported the successful laser etching of polymers, which in their virgin state exhibit no photoetching characteristics, utilizing a methodology known as "doping" [6–9]. In these doping studies, both non-absorbing host matrix and dopant, typically a low-molecular weight and highly conjugated organic, are miscible in a common solvent.

Dopant-induced ablation is of great significance because it provides the opportunity to process materials that do not exhibit desirable excimer laser etching characteristics but offer other outstanding properties. An example of a category of polymers which are technologically important and transparent to conventional excimer emissions are the Teflon type fluoropolymers such as poly(tetrafluoroethylene) (PTFE). However, unlike the aforementioned polymers [6–9], PTFE's chemical inertness and extreme processing requirements presents a significant challenge in identifying and incorporating a suitable sensitizing dye. PTFE, whose structural repeat unit is

$$(-CF_2-CF_2-)_n,$$

has only $n\rightarrow\sigma^*$ and $\sigma\rightarrow\sigma^*$ electronic transitions available. These are high-energy transition requiring short wavelength radiation in order to achieve excitation. Sorokin and Blank have reported that the absorption of UV radiation at wavelengths greater than 140 nm by PTFE is negligible [10]. However, it is worthwhile noting that Kuper and Stuke [11] have discussed the successful etching of PTFE at 248 nm using femtosecond laser pulses in which the ablation process was attributed to multi-photon effects.

Commonly known dopants do not offer the required characteristics, e.g., thermal stability, to behave as effec-

tive sensitizers for fluoropolymers such as PTFE. Polyimides, which are high-performance dielectrics themselves, offer high thermal stability in addition to good absorbing characteristics at common excimer wavelengths and, thus, are ideal dopant candidates for enhanced Teflon ablation. In this paper, we report the successful laser etching of PTFE, using polyimide as a dopant, at 308 nm using fluences ranging from 1–12 J/cm^2 and pulse durations of 25 ns (FWHM).

1 Experimental

1.1 Materials

Biphenyl tetracarboxylic acid dianhydride/phenylene diamine (BPDA–PDA) polyamic acid, Fig. 1a, 14.5% solids in N-methyl-2-pyrrolidone (NMP), TEF 30B, 60% solids PTFE in an aqueous dispersion from E. I. Du Pont de Nemours Co., and 40% dimethyl amine (DMA) in water from Aldrich were used as received. Films of 50 μm Upilex-S polyimide (BPDA–PDA) were obtained from Imperial Chemical Industries, Wilmington, DE.

1.2 Film Formation

Water is a non-solvent for the BPDA–PDA polyamic acid. Thus, in order to successfully introduce it into the PTFE dispersion, water compatibility is required. This was achieved by preparing the organic salt of the polyamic acid. Specifically, the organic salt of BPDA–PDA was obtained by partially reacting the acid functionalities on the polyimide precursor with a suitable organic base, such as DMA. Once formed, the salt, Fig. 1b, was freely added to the aqueous PTFE dispersion. Polymer films, 100 μm thick, of PTFE containing 0, 5, 10, and 15% (wt/wt)

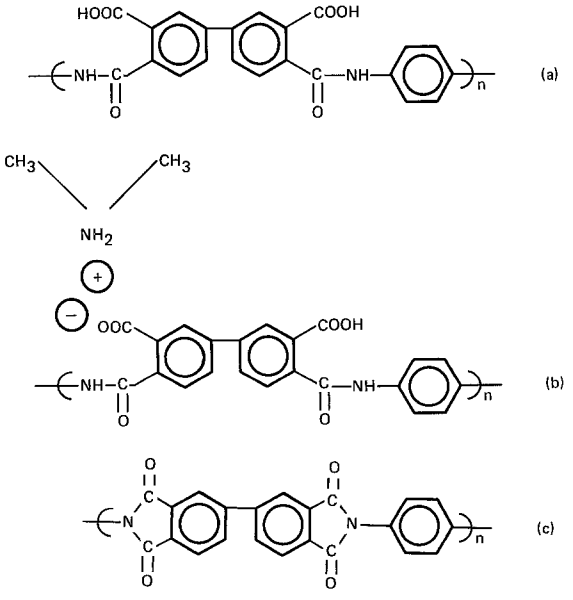

Fig. 1a–c. Structures of repeat units for the BPDA–PDA polyamic acid (**a**), BPDA–PDA polyamic acid salt (**b**), and BPDA–PDA polyimide (**c**)

Table 1. Bake/Cure cycle utilized for film formation

Temperature [° C]	Time [min]
100	60
200	60
320	120

polyimide were prepared using a draw-down bar coater to apply the solution onto a metal substrate. Once applied, the coatings were baked in a Blue M high temperature convection oven, as described in Table 1, to remove solvent and dispersion medium and to thermally imidize the polyamic acid to polyimide, Fig. 1c.

Following the bake, the samples were laminated at high temperature and pressure in order to provide material sintering.

1.3 Excimer Laser Ablation

Ablation of polymers was performed using a Lambda Physik model 203 MSC XeCl excimer laser that emits at 308 nm with a pulse width (FWHM) of 25 ns. A uniform spot intensity profile was obtained using a beam homogenizer built by XMR, Inc. The rectangular homogenized spot was focused onto a stainless steel mask having an aperture whose diameter was 1.27 mm. Fluence was controlled by adjusting the homogenizer which changes the cross-sectional area of the rectangular beam. This does not alter the total energy in the beam at the mask. Fluence was determined by measuring the energy of the beam exiting the mask using a Laser Precision RjP-700 series energy probe. The beam was then directed through a 10× set of reducing optics and focused at the polymer surface. Resulting hole diameter was $\cong$127 μm. A 5 × 10 array of holes was formed in the polymer.

1.4 Analysis

Etching rates were determined from measurements of etching depth using a Sloan Dektak IIA profilometer. The rates are reported as an average of five measurements at randomly chosen positions. Scanning electron micrographs were used to evaluate photo-structuring quality. A Perkin Elmer Systems 7 thermogravimetric analyzer was used to evaluate the thermal stability of the polyimide, using a heating rate of 10° C/minute in N_2. Absorption coefficient evaluations of the polyimide dopant were performed on a dual-beam Perkin Elmer Lambda 9 UV/VIS spectrophotometer using spectroscopic grade quartz wafers as the film substrate and blank.

2 Results and Discussion

Polyimide was chosen as a dopant for PTFE due, in part, to its high thermal stability and strong absorption coefficient, α, at 308 nm. The onset of degradation for

BPDA–PDA in a N_2 atmosphere is in excess of 600° C, as determined from thermogravimetric analysis. The necessity for the fluoropolymer dopant to have high thermal stability, in addition to excellent absorption characteristics, is due to the stringent processing requirements of Teflon polymers, especially PTFE. For instance, PTFE has a crystalline melt temperature, T_m, of $\cong 327°$ C. Figure 2 shows the absorbance spectrum of the BPDA–PDA polyimide. At 308 nm, $\alpha_{BPDA-PDA} \cong 1 \times 10^5\ cm^{-1}$, which is in excellent agreement with the value reported by Liu et al. [12] for polyimides.

Although polyimides offer the required physical characteristics to behave as a sensitizer for Teflon type fluoropolymers, in order to behave effectively as a dopant, it is necessary for the polyamic acid to be aqueous compatible. Water is a non-solvent for the polyimide precursor, and the PTFE component of the coating solution exists in an aqueous dispersion. By forming the aqueous compatible organic salt of the polyamic acid, uniform incorporation of the dopant into the non-absorbing PTFE matrix was achieved, resulting in excellent laser etching behavior. For instance, at 308 nm and a fluence of 12 J/cm^2, excimer laser etching of PTFE is not observed. However, once a small quantity of polyimide is incorporated into the matrix, ablation readily occurs. Figure 3 shows representative SEM photomicrographs of PTFE films containing 5, 10, and 15% polyimide and

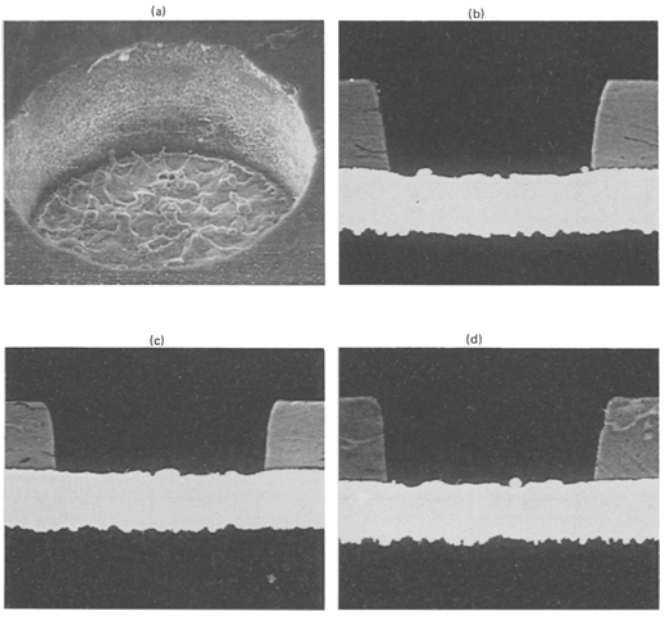

Fig. 3a–d. SEM micrographs of polyimide-doped PTFE films ablated at 12 J/cm^2: 5% polyimide-doped PTFE etched to a metal substrate and shown at 45° (**a**), and cross-sections of drilled holes in composite films doped with 5% (**b**), 10% (**c**), and 15% (**d**) polyimide. In all cases, ablated hole diameters, as measured at the polymer surface, are $\cong 127$ μm

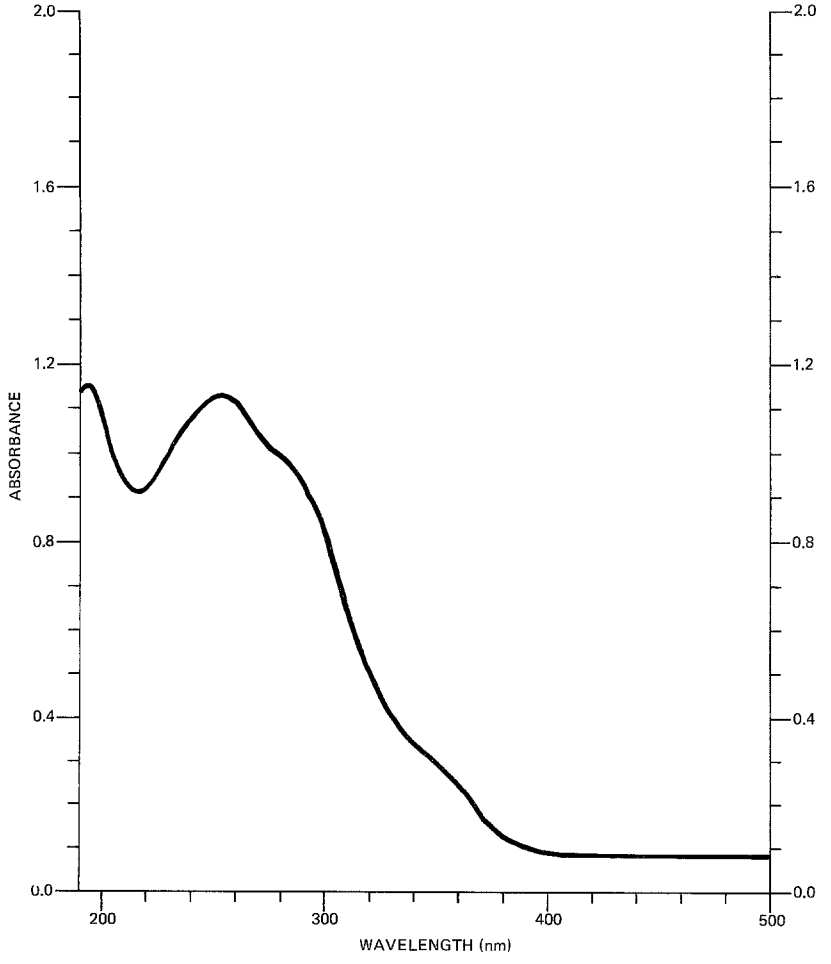

Fig. 2. Absorbance spectrum of the BPDA–PDA polyimide

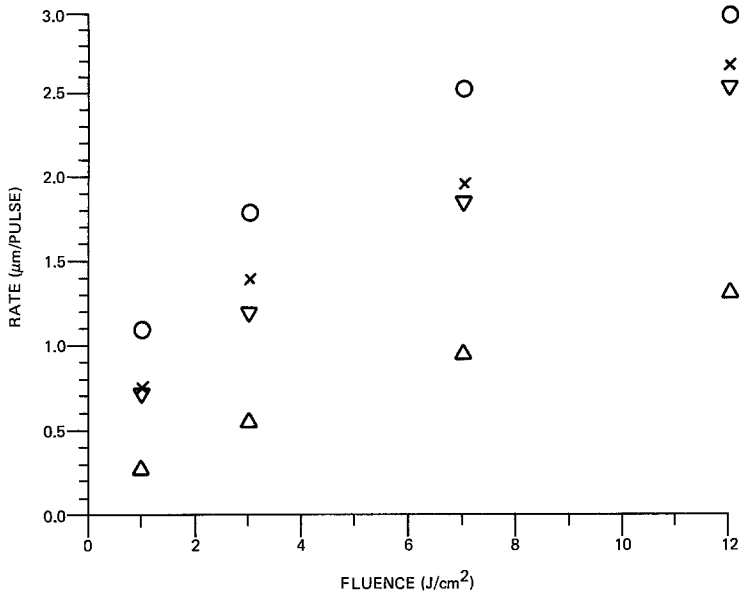

Fig. 4. Effect of dopant concentration on ablation rates between 1 and 12 J/cm^2 for 5% (○), 10% (×), and 15% polyimide (▽). Rates for Upilex-S polyimide are shown for comparison (△)

drilled at 12 J/cm^2. The films' homogeneity, lack of entrance deformation, and smooth sidewalls are readily apparent and was evident at all fluences and dopant concentrations investigated. Such ablation characteristics are indicative of homopolymers that have strong absorption coefficients at the excimer etching wavelength of interest.

Figure 4 illustrates the dependency of the polyimide-doped PTFE films' etch rate on fluence and composition. While the PTFE homopolymer does not exhibit ablation at the conditions investigated, upon incorporation of polyimide, significant etching of the PTFE matrix readily occurs. For example, at a dopant level of 5% polyimide and a fluence of 12 J/cm^2, etch rates in excess of 3 μm/pulse are obtained. Although etch rates are similar for each of the three compositions, in the fluence range investigated, higher dopant concentrations consistently provided decreased etching rates. However, since pure PTFE does not ablate under these conditions, some maximum rate must exist at a polyimide dopant concentration $\leqq 5.0\%$. Ablation behavior of PTFE films at lower dopant concentrations is the subject of a separate investigation. Finally, the polyimide-doped PTFE films' etch rates are significantly greater than that of either homopolymer constituent, PTFE or BPDA–PDA, at all fluences investigated. This concept of an optimum α is in agreement with results of Chuang et al. [8] for dopant-induced ablation of PMMA.

3 Conclusions

In summary, the present study reports the successful excimer laser ablation of PTFE under conventional conditions using polyimide as a doping compound. More specifically, it was found that successful incorporation of small quantities of BPDA–PDA polyimide into the non-absorbing matrix of PTFE have been achieved utilizing the organic salt of the polyimide precursor. The polyimide-doped PTFE films have excellent excimer laser structuring quality, comparable to strongly absorbing polymers, at 308 nm and all fluences investigated. Finally, the doped PTFE films' etch rates are significantly greater than either homopolymer constituent and their respective sums.

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References

1. Y. Kawamura, K. Toyoda, S. Namba: Appl. Phys. Lett. **40**, 374 (1982)
2. R. Srinivasan, V. Mayne-Banton: Appl. Phys. Lett. **41**, 578 (1982)
3. G.D. Mahan, H.S. Cole, Y.S. Liu, H.R. Philipp: Appl. Phys. Lett. **53 (24)**, 2377 (1988)
4. R. Sauerbrey, G.H. Pettit: Appl. Phys. Lett. **55 (5)**, 421 (1989)
5. R. Srinivasan, E. Sutcliffe, B. Braren: Laser Chem. **9**, 147 (1988)
6. H. Hiraoka, T.J. Chuang, K. Masuhara: J. Vac. Sci. Technol. B **6 (1)**, 463 (1988)
7. R. Srinivasan, B. Braren: Appl. Phys. A **45**, 289 (1988)
8. T.J. Chuang, A. Modl, H. Hiraoka: Appl. Phys. A **45**, 277 (1988)
9. H. Hiraoka, S. Lazare: Appl. Surf. Sci. **46**, 342 (1990)
10. O.M. Sorokin, V.A. Blank: Zh. Prikl. Spectrosk. **9**, 827 (1968)
11. S. Kuper, M. Stuke: Appl. Phys. B **44**, 199 (1987)
12. Y.S. Liu, H.S. Cole, H.R. Philipp, R. Guida: Symp. Proc. SPIE **774**, 133 (1987)