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Dopant-Induced Excimer Laser Ablation of Poly(tetrafluoroethylene)

II. Effect of Dopant Concentration

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Abstract. Clean ablation of poly(tetrafluoroethylene) (PTFE) at etch rates in excess of 7 μm/pulse has been achieved with an excimer laser using 308 nm radiation and a 25 ns pulse width. This was accomplished by doping the ultraviolet-transparent PTFE polymer with polyimide. Ablation rates were investigated as a function of fluence in the range from 1 to 12 J/cm^2 and dopant levels up to 15% (wt/wt). Results show that at a given fluence there exists an optimum absorption coefficient α_{max}, for which maximum ablation rates are achieved. The value of α_{max} was found to decrease with increasing fluence. The relationship between α_{max} and fluence was determined from existing ablation rate models and found to compare favorably with empirical results.

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Early investigations of controlled polymer structuring by high-energy ultraviolet (UV) laser radiation [1, 2] utilized materials that had inherent photon absorption at the wavelength studied. For instance, ablation of poly(ethylene terephthalate) (PET) [1] and poly(methyl methacrylate) (PMMA) [2] was investigated at 193 nm. Subsequent work included ablation of materials that absorbed at longer wavelengths, such as polyimide at 308 nm [3–6].

For ablation to occur, the material must absorb photons. The depth of photon absorption by a medium typically follows Beer's law,

$$A = abc, \tag{1}$$

where A is the wavelength-dependent absorption, a is the absorptivity, b is the path length of radiation through the medium, and c is the chromophore concentration. A is dimensionless, thus a requires units that render the right side of equation (1) unitless. In studies of polymer film ablation, it is often convenient to describe the interaction of the emitted laser energy with the material in terms of absorption coefficient, $\alpha = A/b$.

Not all polymers have the requisite chemical functionality their molecular structure to inherently absorb the high-energy UV photons as required for excimer laser ablation. For instance, PMMA is not readily structured at 308 nm. However, several researchers have reported successful excimer ablation of UV-transparent materials using a technique known as "doping" [7–11]. In these investigations, a low-molecular weight, highly conjugated organic compound that absorbs strongly at the excimer laser wavelength of interest is incorporated into the non-absorbing host matrix. As a result, absorption of UV radiation by the doped polymer occurs leading to ablation. One example is structuring of PMMA doped with pyrene using 308 nm exposure [7–9]. A common characteristic of doping investigations to date has been that the dopant and UV-transparent polymer have similar solubility characteristics, simplifying fabrication of the compositions and ensuring even and uniform incorporation of the sensitization agent into the non-absorbing matrix. However, dopants and sensitization techniques commonly found in the literature cannot be extended to UV-transparent polymers which are chemically inert (insoluble) or require extreme processing conditions (high temperature). One such UV-transparent polymer is poly(tetrafluoroethylene) (PTFE).

Clean ablation of neat PTFE has only been achieved using very short pulses (e.g., femtosecond pulse width) [12] to provide high-intensity radiation, or using shorter wavelengths than commonly produced with commercially available excimer lasers [13]. However, Davis et al. [14] recently reported the successful etching of PTFE at 308 nm and a pulse duration of 25 ns by doping the fluoropolymer with polyimide. In that study, dopant levels between 5% and 15% polyimide were investigated in a fluence range of 1 to 12 J/cm^2 with resulting ablated features being well defined and comparable in quality to that of good absorbing homopolymers. In addition, in the range of fluence levels investigated, the ablation rate of the blend was greater than those for either homopolymer (PTFE or polyimide film). It was also observed that at a given fluence, the ablation rate of the blends increased with decreasing dopant concentration. Hence, a maximum rate must exist at some dopant concentration between 5% polyimide (the lowest

concentration used in that study) and neat PTFE (which does not etch). This concept of an optimum dopant level, in terms of ablation rate, is consistant with behavior reported for polymers doped with low-molecular weight organics [9]. The purpose of this paper is to present results of a continued investigation of the polyimide/PTFE system at lower dopant levels than previously reported [14].

1 Experimental

Details of material preparation, ablation and analysis were reported in [14].

Biphenyl tetracarboxylic acid dianhydride/phenylene diamine (BPDA-PDA) polyamic acid, 14.5% solids in *N*-methylpyrrolidone (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[1] polyimide (BPDA-PDA) were obtained from Imperial Chemical Industries, Wilmington, DE.

Polymer films, 100 µm thick of PTFE containing 0, 0.1, 0.2, 0.3, 0.5, 1.0, 5.0, 10.0, and 15.0% (wt/wt) polyimide were prepared using a draw-down bar coater to apply an aqueous dispersion of the PTFE dispersion and polyamic acid salt onto a metal substrate. Once applied, the coatings were baked in a Blue M high-temperature convection oven to remove solvent and dispersion medium and to thermally imidize the polyamic acid to polyimide. Following the bake, the samples were laminated at high temperature and pressure in order to provide material sintering.

Due to the inherent crystalline nature of PTFE, accurate measurement of its absorption coefficient, α_{PTFE}, is difficult.

[1] Upilex-S is a registered trademark of Ube Industries, Ltd., Tokyo, Japan

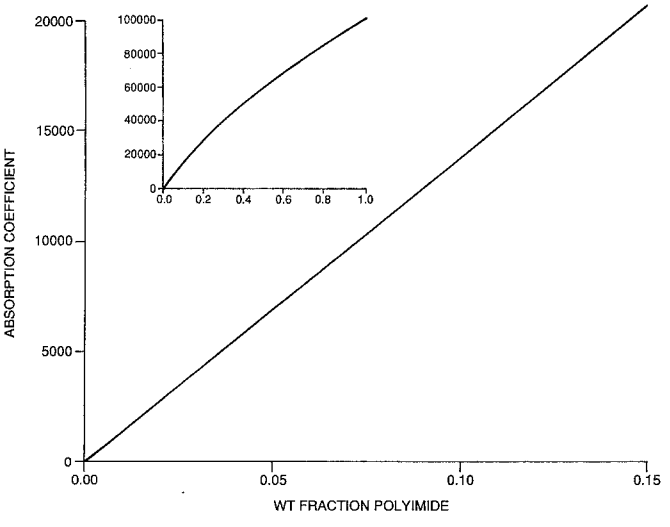

Fig. 1. Absorption coefficient at 308 nm for polyimide/PTFE blends predicted using a rule of mixtures relationship for polyimide dopant concentrations (weight fraction of polyimide) up to 15%. Calculated values of α_{blend} over the full range of polyimide concentrations, from neat PTFE to neat polyimide (Upilex-S film) are given in the inset

Hence, determination of absorption coefficients for various blends is equally challenging and their experimental values are not reported here. However, literature values for α_{PTFE} are reported to be less than $10^1\,cm^{-1}$ [15] at 308 nm, in comparison with polyimide for which α is on the order of $10^5\,cm^{-1}$. There is no alteration of the molecular structure of host or dopant upon mixing. In addition, it has been reported that there is no electronic interaction between the excited dopant and the host polymer [9]. Therefore, a rule of mixtures relationship is used to predict α_{blend}. Variation in α_{blend} with polyimide dopant concentration is shown in Fig. 1.

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 homogenized spot was focused onto a stainless steel mask having an aperture with a 1.27 mm diameter, and then directed through a 10X set of reducing optics and focused at the polymer surface. Resulting hole diameter was $\cong$ 127 µm. Drilling rates were determined from measurements of etching depth using a Sloan Dektak IIA profilometer. The rates are reported as an average of measurements at five positions.

2 Results and Discussion

Etch rates as a function of laser fluence are shown for a variety of polyimide/PTFE blends in Fig. 2. Shown for comparison is the etch rate of Upilex-S polyimide film. Under the experimental conditions, ablation is not observed for neat PTFE or the 0.1% doped blend. Etch rates for all other compositions exhibit the logarithmic-type behavior of many polymer ablation processes, i.e., a rapid increase at fluences just above the threshold with a more gradual increase at higher levels.

At the highest fluence levels investigated ($> 3\,J/cm^2$), ablation rates for the blends increase with a decreasing polyimide level until a maximum is achieved at a dopant concentration near 0.2%. At 0.2% polyimide and a fluence

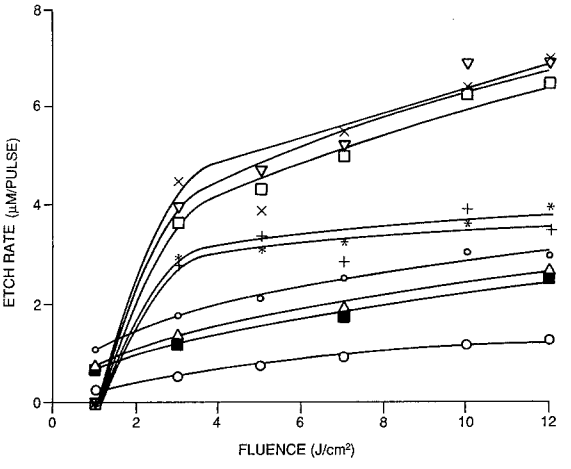

Fig. 2. Etch rate of PTFE with various doping levels as a function of fluence; 0.2% (×), 0.3% (▽), 0.5% (□), 0.75% (∗), 1.0% (+), 5.0% (○), 10.0% (△), 15% (■), and Upilex-S film (◯)

of 12 J/cm^2, an etch rate greater than 7 μm/pulse is achieved, higher than values typically reported in the literature for most homopolymers. In addition, ablation rates for blends near this dopant concentration continue to increase significantly with increasing fluence, especially in comparison with the more heavily doped blends and neat polyimide. Ablation rates for the blends at 7 J/cm^2 are shown as a function of polyimide dopant concentration in Fig. 3. The presence of an optimum dopant concentration occuring near 0.2% is evident. This is consistent with the trend reported earlier for higher polyimide concentrations [14].

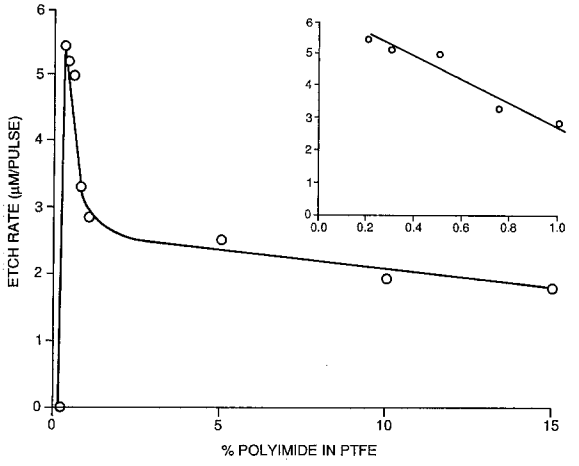

Fig. 3. Etch rate as a function of dopant concentration (up to 15%) at 7 J/cm^2. The inset shows the same data plotted up to 1.0% polyimide (excluding 0.1%)

Figure 4a shows an SEM micrograph (in cross section) of a feature ablated in doped PTFE, specifically 0.5% polyimide at 12 J/cm^2. The ablated feature is well defined and exhibits a smooth wall profile, typical of all blends having $>0.1\%$ polyimide. The sidewall profiles of the less heavily doped blends are extremely vertical, having less taper than typically observed for more heavily doped PTFE films, 1.0% and 5.0%, respectively (Figs. 4b, 4c), or for Upilex-S polyimide (Fig. 4d). This dependence of wall taper on absorption coefficient or dopant concentration in transparent matrices is not fully understood at this time.

Unlike α_{blend}, ablation rates cannot be calculated directly from a simple rule of mixtures relationship. However, rates calculated by this means offer a baseline for comparing the relative enhancement due to doping. Etch rates depend on α and follow more complex equations, such as those developed by several investigators and discussed in more detail below [5, 16, 17]. In fact, the etch

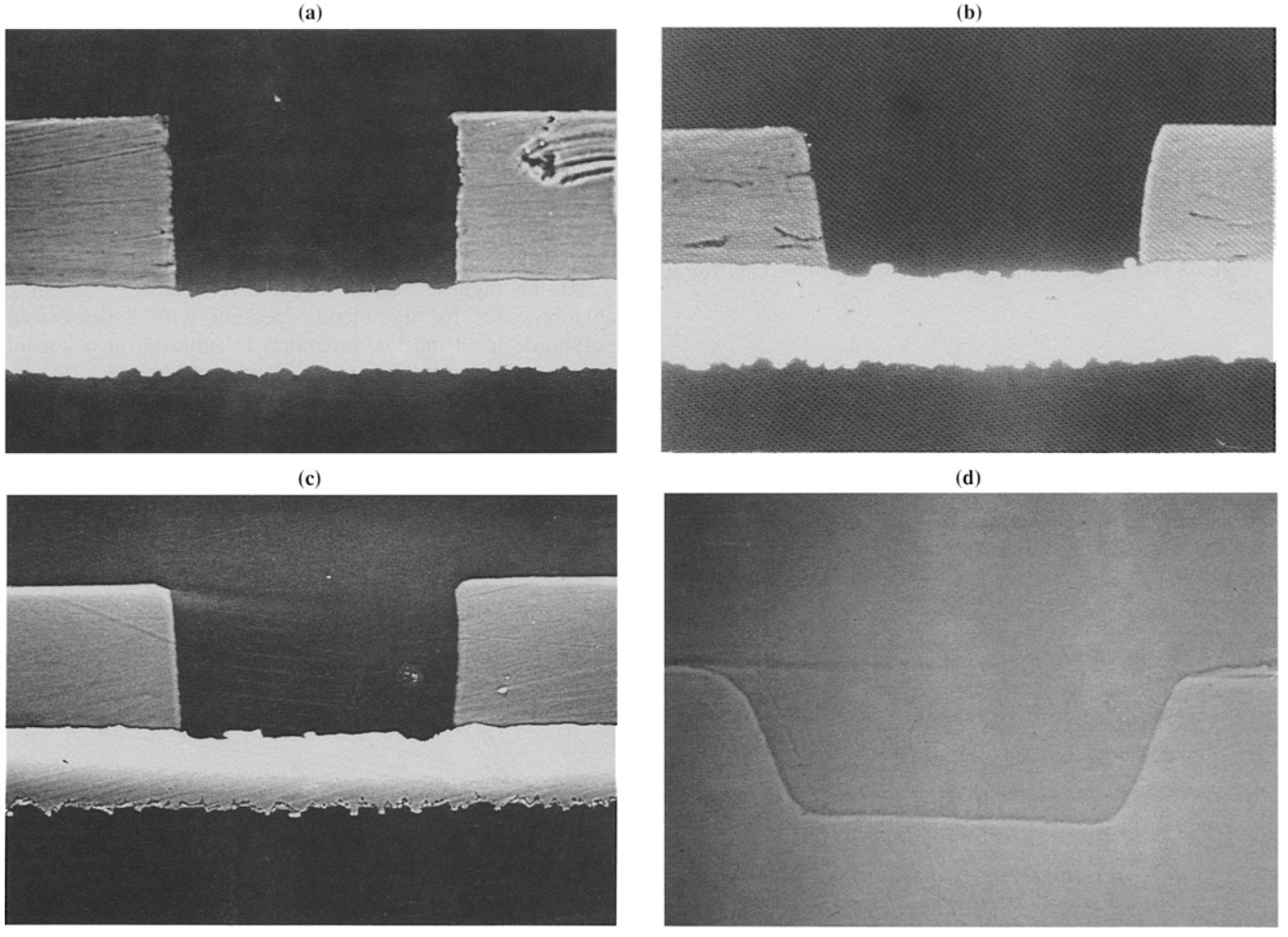

Fig. 4a–d. SEM micrographs of laser etched PTFE doped with polyimide at concentrations of 0.5% **(a)**, 1.0% **(b)**, and 5.0% **(c)**, and polyimide **(d)**. Fluence was 12 J/cm^2

Table 1. Comparison of ablation rates (μm/pulse) for various PS/PMMA blends with those for their constituent homopolymers [18]. The number in parentheses indicates the ratio of the measured rate of the blend to a rate predicted based on a simple rule of mixtures

	Fluence [J/cm^2]		
	0.1	0.2	0.4
PS	0.08	0.10	0.18
PMMA	0.07	0.19	0.42
2% PS in PMMA	0.15 (2.1)	0.33 (1.7)	0.40 (1.0)
20% PS in PMMA	0.13 (1.9)	0.21 (1.2)	0.27 (0.7)

Table 2. Comparison of ablation rates (μm/pulse) for various polyimide/PTFE blends with those for their constituent homopolymers. The number in parentheses indicates the ratio of the measured rate of the blend to a rate predicted based on a simple rule of mixtures

	Fluence [J/cm^2]		
	1.0	7.0	12.0
PTFE	0	0	0
Upilex-S	0.27	0.95	1.3
0.2% polyimide/PTFE	0 (0)	5.5 (1800)	7.0 (1750)
5.0% polyimide/PTFE	1.1 (55)	2.5 (35)	3.0 (33)

rates of the polyimide/PTFE blends are orders of magnitude greater than those predicted from the rule of mixtures based on volume percent concentrations of the individual constituent homopolymers. This phenomenon has not been previously discussed for any dopant/polymer system. Cole et al. [18] investigated polymer blend ablation at 193 nm of PMMA doped with poly(α-methylstyrene) (PS). However, unlike the present system, both PS and PMMA possess appreciable absorption at 193 nm, $8.0 \times 10^5\,\mathrm{cm}^{-1}$ and $2.0 \times 10^3\,\mathrm{cm}^{-1}$, respectively [18]. Experimental ablation rates for the PS/PMMA blends, PMMA and polystyrene are shown in Table 1 with calculated rates for the blends using a rule of mixtures assumption. In the fluence range investigated, the etch rates for the blends are as much as two times greater than that predicted using a rule of mixtures rate relationship.

Table 2 contains similar data analyses derived from Fig. 2 of the present study. Since PTFE is transparent at 308 nm, a very large enhancement is obtained, in some instances a factor of $\cong 2 \times 10^3$. Larger enhancements are not observed for the PS/PMMA system (Table 1) since each homopolymer exhibits significant absorption at the wavelength investigated. For the polyimide/PTFE system, greatly enhanced ablation rates are achieved at low dopant levels where significant changes in other physical or chemical properties of PTFE are not observed. For example, dielectric constants for neat PTFE and a blend of 5% polyimide and PTFE are 2.10 and 2.15, respectively [19]. In addition, thermogravimetric analyses show that thermal decomposition of the blends is equivalent to that of neat PTFE [20].

It is observed that in the low fluence region ($< 3\,\mathrm{J/cm}^2$), blends having higher dopant levels are required to achieve maximum etch rates. The distinction between low and high fluence regimes is somewhat arbitrary, but is identified here as the fluence region where the rate vs fluence curves, for materials having different absorption coefficients, cross. This behavior has been observed for other doped systems [9, 11]. The fluence value at which this phenomenon occurs is dependent upon the polymer matrix and absorption coefficient (as determined by wavelength and dopant concentration). For the present system, it is expected that further reducing fluence would lead to a condition for which Upilex-S polyimide would exhibit a greater rate than any of the polyimide/PTFE blends. At $1\,\mathrm{J/cm}^2$ the maximum rate occurs near 5.0% polyimide, in comparison with the observation of maximum rates occuring for 0.2% dopant level at higher fluences. Estimates of α_{blend} using the rule of mixture are $3.0 \times 10^2\,\mathrm{cm}^{-1}$ and $7.2 \times 10^3\,\mathrm{cm}^{-1}$ for 0.2% and 5.0% polyimide dopant concentrations, respectively (Fig. 1). This dependence of optimum absorption coefficient (in terms of ablation rate) α_{max} on fluence is consistent with the observations of Chuang et al. [9] for ablation of several UV-transparent (308 nm) polymers sensitized with low-molecular weight dopants, e.g., PMMA doped with pyrene. For the pyrene/PMMA system, Chuang et al. [9] reported maximum etch rates for $1.2\,\mathrm{J/cm}^2$ at $\alpha = 7 \times 10^2\,\mathrm{cm}^{-1}$. It should not be expected that different dopant/polymer systems would yield the same optimum absorption coefficient for a given fluence level since the thermal properties for the different polymers may vary significantly.

Fast, clean ablation of PTFE blends for which α is on the order of 10^2 and using low intensity irradiation may, at first, seem inconsistent with the lack of ablation reported for neat PTFE at 193 nm [13] where α_{PTFE} has been measured using a vacuum UV spectrometer to be 2.6×10^2 [15]. In addition, Kuper and Stuke [12] observed that single photon ablation of PTFE did not occur at 248 nm where α_{PTFE} was reported to be 1.4×10^2. However, for PTFE, the difference in energy between the highest occupied molecular orbital and the lowest antibonding orbital, $n \rightarrow \sigma^*$, is so large that single-photon electronic excitation requires a photon energy roughly equal to the ionization potential [21, 22] (on the order of 11 eV, as determined by valence band X-ray photoelectron spectroscopy [23]). In fact, irradiation of PTFE through crystal filters having various cut-off wavelengths suggests that PTFE modification, which in this configuration requires photon absorption, does not occur for radiation greater than 160 nm [23, 24], i.e., energies around 7.8 eV. This is consistent with observed ablation of PTFE using an F_2 laser operating at 157 nm [13]. Hence, at wavelengths greater than or equal to 193 nm, the absorption coefficient of neat PTFE must be zero. Reported values of $\alpha_{\mathrm{PTFE}} > 0$ at commonly available excimer laser wavelengths may, in large part, be attributed to scattering due to crystalline regions and/or impurities in the polymer.

At low fluence levels, several studies [3, 16, 17, 25] have found the relationship

$$l = (1/\alpha)\ln(F/F_{\mathrm{Th}}) \tag{2}$$

to be suitable for predicting how etch rate l varies with fluence F and the threshold fluence F_{Th}. In this fluence

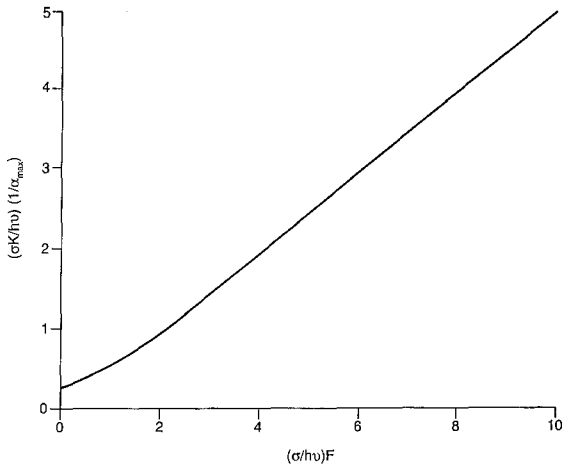

Fig. 5. Plot of $(\sigma K/h\nu)(1/\alpha_{max})$ vs $(\sigma/h\nu)F$ demonstrating the inverse relationship between α_{max} and F

region, the relationship between fluence and α_{max} can be derived using (2). Several investigations have shown that F_{Th} decreases as α increases [3, 9, 16]. Jellineck and Srinivasan [16] derived the simple relationship

$$\alpha F_{Th} = K\,, \tag{3}$$

where K is a constant. Although a polymer degradation rate constant k_1 is incorporated into K, neither k_1 nor K should vary with small changes in dopant concentration. The actual relationship between α and F_{Th} is probably somewhat more complex than stated in this simple expression. In fact, Chuang et al. [9] have shown that although the product of α and F_{Th} is not constant, there is certainly a reciprocal dependence between these two terms. Further departures from the simple relationship may, in part, be due to ambiguities in F_{Th} measurements. Nevertheless, using (2) and (3) and setting $d/d\alpha$ equal to zero to solve for α_{max} yields $\alpha_{max} \propto 1/F$, consistent with empirical observations.

Deviations between actual ablation rates and those predicted using equation (2) occur at higher fluences [17, 25]. Hence, a different rate equation is required to determine the relationship between α_{max} and fluence. Using a rate model proposed by Srinivasan et al. [17] to determine this relationship requires a knowledge of certian empirically determined physical parameters to find the dependence of α_{max} on F. Since these parameters are not presently known for the polyimide/PTFE blends, this was not pursued. However, a rate model proposed by Sauerbrey and Pettit [5] requires no such information. In this model, the etch depth per pulse is given by

$$l = (1/\varrho_0)(S_0 - S_{Th}) + (1/\alpha)\ln[(1 - e^{-\sigma S_0})/(1 - e^{-\sigma S_{Th}})]\,,$$

where ϱ_0 is the density of light absorbing chromophores in the material, S_0 is the photon density at the surface, S_{Th} is the threshold photon density, and σ is the single photon cross section; $\sigma = \alpha/\varrho_0$, a constant in the present investigation. Fluence and photon density S are related according to $F = h\nu S$ where $h\nu$ is the photon energy. Setting $d/d\alpha$ equal to zero yields

$$\ln(1 - e^{-u}) + u[2 + (e^u - 1)^{-1}] = \ln(1 - e^{-w}) + w\,, \tag{4}$$

where

$$u = (\sigma K/h\nu)(1/\alpha_{max})$$

and

$$w = (\sigma/h\nu)F\,.$$

At higher fluence levels (but in a range where single-photon absorption still dominates), the first term on the right side of (4) is negligible. Since σ and K are specific to a given polymer and not known *a priori*, values for u have been arbitrarily chosen and substituted into (4) to determine w. A plot of w vs u (Fig. 5) reveals that α_{max} and F have an inverse relationship for all values of α_{max} and F.

3 Conclusions

Doping of PTFE allows clean ablation at extremely high rates without significant changes in other physical or chemical properties. For the polyimide/PTFE blend systems, etch rates substantially greater than those of the individual homopolymers and those predicted from a simple rule of mixtures are achieved. An optimum absorption coefficient α_{max}, which yields a maximum ablation rate at a given fluence F has been observed and is in agreement with previous results obtained with low-molecular weight dopants in other polymers that are transparent at the particular excimer laser wavelength studied [9]. Several ablation rate models have been used to show that α_{max} and F have an inverse relationship. Although this result is in agreement with trends observed in the present study and in the literature, the exact relationship between α_{max} and F has not been verified.

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