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Determination of laser ablation threshold of Teflon at different harmonics of Nd:YAG laser using photothermal deflection technique

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We report the measurement of the laser ablation threshold of Teflon using photothermal beam deflection at 1.06 μm, 0.532 μm, and 0.355 μm irradiation in air. The measured ablation threshold at various wavelengths is used to estimate the absorption coefficient. It is observed that the absorption coefficient increases with a decrease in wavelength.

1. Introduction

Interaction of lasers with polymers has gained interest in the last several years because of their wide use in the microelectronics industry and as optical materials. Interaction of lasers with organic polymers is different from that of metal and semiconductors. The absorption of UV photons by organic molecules leads to electronic excitation whereas infrared photons lead to vibrational and rotational excitation. The reactions that the electronically excited molecules subsequently undergo are so varied and dependent upon the chemical structure of the molecule, the wavelength of the photon and the medium in which the reaction is carried out that the study of organic photochemistry has evolved over the past several years into a field in itself. Srinivasan *et al*. [1, 2] have studied extensively the process of laser interaction with organic polymer materials in the different wavelength regions. They have shown that there are two distinct processes, one photochemical and another photothermal, which take place during the laser interaction with the polymer materials [3]. Photochemical absorption dominates in the UV region, resulting in the dissociation of the molecule to the ground state. Longer wavelength light is absorbed into the vibrational modes of the molecule either directly or indirectly via low lying electronic states.

Research on ablation and etching of organic polymers by pulsed UV laser irradiation has focused mostly on three polymers: namely, polymethyl methacrylate (PMMA), polyimide (Kapton), and polyethylene terepthalate. Of these, PMMA has attracted significant attention. Beside these polymers, Teflon is another useful commercial polymer. Recently there have been reports of making microlens arrays from the doped Teflon [4]. However, there is hardly any work reported on the interactions of laser beams with Teflon. Further, a necessary criterion for a material to be of wide use is that it should have a high damage threshold [4]. Thus, it is necessary to know its ablation threshold. Several mathematical models on laser-polymer interactions exist in the literature. Jellinek *et al*. [5] established a functional relationship between etch depth and incident fluence on the basis of polymer degradation kinetics. Srinivasan *et al*. [6] proposed a model of polymer ablation due to a combination of photochemical and photothermal processes. At low fluences the model reduces to that derived by Jellinek *et al*. In more recent work, Srinivasan [7] has reported a comparative study of the ablation of PMMA film by pulsed (nsec) UV and IR (9.17 μm) lasers. The quantitative treatment which is widely accepted to analyse experimental data is based on Beer's law;

$$x_f = (1/\alpha) ln(F/F_0) \tag{1}$$

This expression gives the analytical relation between the etch depth per pulse x_f, the absorption coefficient α, the laser fluence F and the threshold fluence F_0. The linear relationship between x_f and lnF holds generally only in a very narrow fluence range. The slope of the plot is invariably different from $1/\alpha$ over a wide range of fluence. This approach has two major weak points; it implicitly assumes that ablation occurs after the pulse has travelled through the sample; and secondly the time scale in which the laser light is delivered to the sample is irrelevent. The first point contradicts the stress pulse measurements [8] and is not consistent with simulation of UV laser ablation [9] based on the solutions of the classical equations of motion which predict the onset of ablation only a few picoseconds after the bond breaking step. The second point is clearly unrealistic. To explain the experimental results a kinetic model of photoablation based on the moving interface has been proposed by Lazare *et al*. [10, 11].

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The model gives the rate of ablating interface equal to k(I-I_t) for I > I_t and zero for I < I_t. I is the instantaneous intensity falling on the moving interface and I_t is the instantaneous ablation threshold intensity; k is the ablation rate constant of the polymer. The intensity that reaches the interface is attenuated by the absorption of the ablating species, $I_0 e^{-\beta x}$, where β is the screening coefficient and x is the position of the interface. Since the threshold for ablation is one of the fundamental parameters for understanding the mechanism of the damage, several methods have been used to determine it. The photoacoustic and photothermal deflection techniques have been developed for studying the thermal damage [12], measuring etch rate and determining the ablation thresholds of different materials. Theoretical models to predict ablation threshold fluence [13] have also been proposed. Oldershaw *et al*. [14] have calculated the laser ablation thresholds for PET at the different wavelengths from UV to IR. Instead of measuring etch depth, Lazare and Granier [15] introduced a more sensitive method of using a microbalance to measure the pulsed UV laser ablation. Techniques like laser induced fluorescence [16], mass spectroscopy [17], and emission spectroscopy [18] have been used to get information about the fragments leaving the surface at supersonic velocities.

Photothermal Deflection Technique (PDT) is a useful and versatile technique for determining damage and ablation threshold of different materials such as polymers, superconductors etc. [19]. The technique essentially consists of measuring the deflection of an optical (probe) beam due to the refractive index gradient in the vicinity of a sample surface generated by a pulsed/modulated beam. In the present communication we report a comparative study of laser ablation threshold measurement for commercial Teflon (Du Pont), with the usual PTFE (Poly Tetra Fluoro Ethylene) structure which is widely used as insulator and heat resistive, at the three wavelengths 1.06 μm, 0.532 μm and 0.355 μm of Nd:YAG laser. The effective absorption coefficients of Teflon at different wavelengths is estimated using the Furzikov formula and thermolysis rate [13].

2. Experimental setup:

A schematic diagram of the experimental setup [20] used for PDT is shown in Fig. 1. We used a low power He-Ne laser (power 0.5 mW) with spot diameter of 1 mm at a distance of 1 meter as a probe beam which passes parallel to and 2 mm away from the target surface. A high power Q-switched Nd:YAG laser

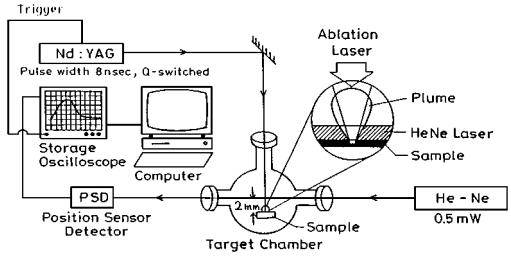


Figure 1 Schematic diagram of the experimental set-up.

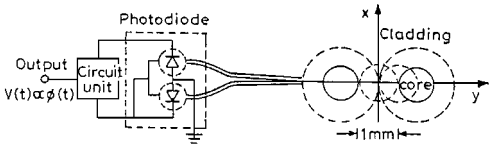


Figure 1a Design of a Bi-cell detector.

of pulse width 8 nsec (FWHM) which has three harmonics (ω_0, $2\omega_0$, $3\omega_0$) is used as a pump beam to heat the surface of the material normal to the probe beam. The pump beam is tightly focused with a convex lens to a diameter of 350 μm on the Teflon target. The laser beam falling on the target is readily absorbed and a fraction of the heat energy is conducted into the adjacent air close to the target surface. The increase in the temperature of the air changes its refractive index. This change of refractive index of the air causes the deflection of the probe beam. Deflection of the probe beam is monitored with the help of an optical fiber coupled bi-cell type position sensor detector. The detector comprises of two optical fibers kept side by side as shown in Fig. 1a and are coupled to the two photodiodes at the other end. The difference in the amount of light due to the deflection of the probe beam is measured by the two photodiodes. The sensitivity of the position sensor detector is 4 mV/μ rad at a distance of 1.25 m. The data was recorded through a storage oscilloscope (Iwatsu, TS 8123). The deflection of the probe beam is given by [19],

$$\phi = \frac{1}{n}\frac{\partial n}{\partial T}\frac{\partial T}{\partial Z}L \tag{2}$$

where n is the refractive index, T the temperature of air, Z is the distance normal to the target surface, and L is the interaction length of the pump and probe beam. For our case $\frac{\partial n}{\partial T}$ is essentially constant, the gas being close to the ambient temperature. To evaluate $\frac{\partial T}{\partial Z}$ one can use the thermal heat conduction and diffusion equation between the boundary of a solid (i.e. the target) and air (or gas). It is assumed that the laser energy is absorbed at the surface of the target (the laser acts as an instantaneous source) and a fraction of the heat energy is conducted into the air which raises its temperature. Following [21] the temperature of the air at time t is given by,

$$T = \frac{K_s D_g D_s^{-1/2}}{\left(K_s\sqrt{D_g} + K_g\sqrt{D_s}\right)\sqrt{\pi D_g t}} \cdot exp - (vt - Z)^2/(4D_g t) \tag{3}$$

where K_g and D_g are the thermal conductivity and thermal diffusivity of the gas respectively, and K_s and D_s are those of the solid. Differentiating Equation 3 and substituting into Equation 2, we get

$$\phi = \frac{1}{n}\frac{dn}{dt}\frac{LF}{4\sqrt{\pi\rho_g C_g}}\sqrt{D_s/D_g}\cdot\frac{(vt - Z)}{(D_g t)^{3/2}} \cdot exp - ((vt - Z)^2/(4D_g t))\cdot(1 + \Gamma)\cdot\frac{K_g}{K_s} \tag{4}$$

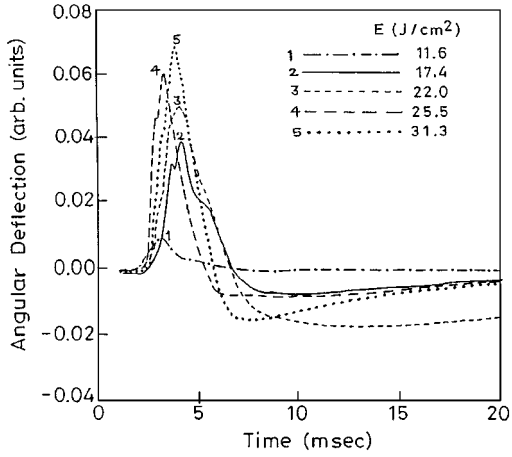


Figure 2 Variation of angular deflection with time.

where Γ is the thermal mismatch defined as $\Gamma = \frac{(e_s - e_g)}{(e_s + e_g)}$ where e_s and e_g are the effusivities of the solid and gas respectively, v the velocity of the air, F the laser fluence, ρ_g density of the gas, C_g the thermal heat capacity of the gas and t is the time. Below the ablation threshold the velocity of the air in the z direction perpendicular to the target surface is taken to be zero, a constant amount of heat is conducted into the air and there is no zero crossing of the angular-deflection time curve. As the fluence of the pump laser crosses the ablation threshold, there will be zero crossing of the curve due to the convective plume of the mixture of gas and ablating material as shown in Fig. 2. Thus by monitoring the zero crossing of the angular deflection-time curve one can infer the ablation threshold of different materials.

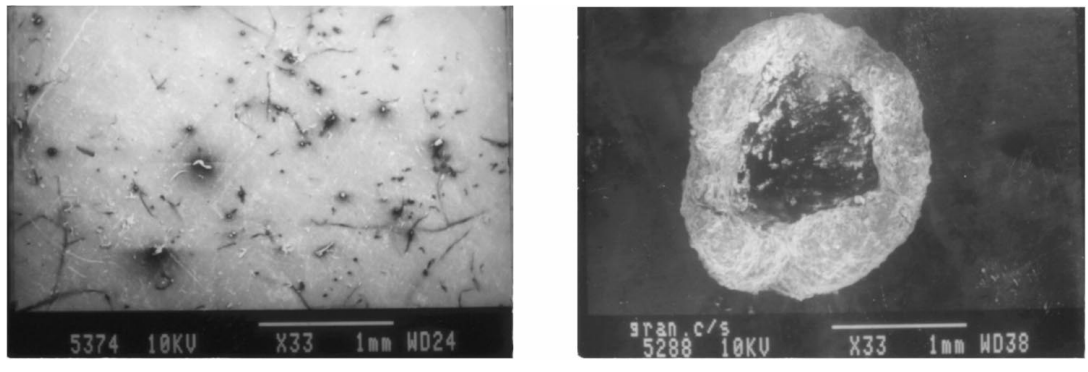
3. Results and discussions:

Fig. 2 shows the deflection of the probe beam for different laser fluences at 0.355 μm. Below the ablation threshold a constant amount of heat is conducted into the air close to the target surface which creates a density gradient. The deflection of the probe beam is solely due to the thermal wave reflected from the target surface resulting in a positive signal. Above the ablation threshold, plasma formation starts creating both neutrals and electrons. The deflection signals represent refraction of the probe beam into the regions of higher

TABLE I Ablation threshold fluences (J/cm^2) and Ablation coefficients (cm^{-1}) of Teflon at atmospheric pressure for Nd:YAG laser and its harmonics

λ (μm)	Threshold fluence (J/cm^2)	Ablation coefficients (cm^{-1})
1.064	60.00	1.61
0.532	40.00	3.63
0.355	17.40	19.18

gas density for a neutral gas (refractive index $n > 1$) and vice versa for the electrons in a plasma ($n < 1$) [22, 23] resulting in a distinct positive signal at earlier times and a negative signal at later times. The zero crossing of the deflection signal corresponds to a sudden change of $n > 1$ to $n < 1$ and hence of the ablation threshold [24]. Therefore from the zero crossing one can estimate the laser ablation thresholds of different materials. The SEM picture of crater formation just above and below the ablation threshold shown in Fig. 3 depicts the damage threshold. We have determined the ablation threshold of Teflon at wavelengths 1.06 μm, 0.532 μm and 0.355 μm. The results are summarized in Table I. The behaviour of the amplitude (peak to peak voltage) of the photothermal deflection signal with the increasing laser fluence shows an abrupt fall in the linear behaviour at the ablation threshold. The nonlinear behaviour may be due to the multiphoton processes which are likely to occur at the wavelength used. The behaviour of the amplitude signal at various laser fluences at different wavelengths of Nd:YAG laser is shown in Fig. 4. As soon as the temperature of a certain layer of the material exceeds a value at which the molecules of the material have sufficient kinetic energy to break the bonds, the ablation sets in. Teflon has a bond energy of 406 kJ/mole corresponding to C–C bonds and 520 kJ/mole for C–F bonds which have to be overcome before ablation can occur [25]. In our experiment we used wavelengths ($\lambda > 340$ nm) where the thermal model is valid [9]. Our observed values of threshold for Teflon are relatively high. This may be attributed to the weak absorbing property of Teflon. The threshold value decreases as we go to the lower wavelengths because of higher absorption at lower wavelengths. This also follows from our observation of the variation of signal amplitude above the ablation threshold where it is



(a) (b)

Figure 3 SEM picture of Teflon just below (a) threshold and above (b) ablation threshold for 1.06 μm. The magnification is 30 times.

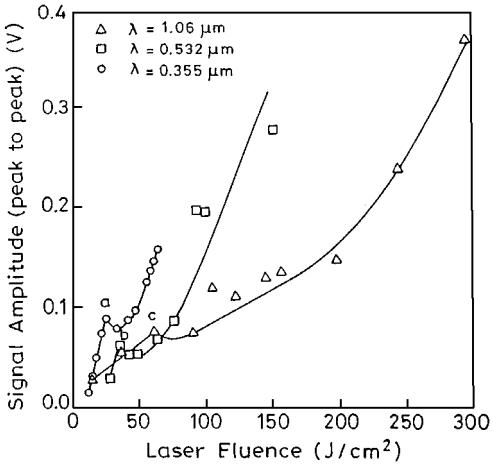


Figure 4 Variation of amplitude (peak to peak voltage) of the angular deflection with laser fluence at different wavelengths. The points marked by a, b and c are the ablation thresholds at the respective wavelengths.

observed that the amplitude rises for lower wavelength more rapidly compared to that of higher wavelength. Also at lower wavelength single photoionization dominates rather than multiphoton ionization. Thus etching is much more efficient in the UV range than in the IR region. To understand the mechanism of the process of absorption and ablation it is important to determine the ablation threshold and effective absorption coefficient (ablation coeffcient). We estimated the absorption coefficients using Arrhenius law of thermal degradation, the heat conduction equation and Furzikov's formula [13]. According to Arrhenius' Law the first order rate constant for thermal degradation of a polymeric material is given by [14],

$$k(sec^{-1}) = Aexp(-E_a/R\Delta T) \qquad (5)$$

where A is the Arrhenius parameter, E_a the activation energy and ΔT is the rise in temperature.

On inserting the Arrhenius equation into the heat conduction equation the percentage of thermal degradation of polymeric material with time can be calculated. Oldershaw *et al*. [14] reported the laser ablation threshold for PET at different wavelengths. Assuming 10 percent of the polymer decomposes at the end of the laser pulse at threshold [14] we calculated the ablation threshold for Teflon at the wavelengths 193 and 157 nm for which the values of the effective absorption coefficient (ablation coefficient) and ablation threshold are known [26]. Using the Arrhenius law one can find the increase in temperature of the material for which 10 percent of the polymer decomposes. The estimated temperature is rather high ($\simeq$2533 K) for Teflon.

According to Furzikov, the laser ablation threshold for low absorbing polymers is given by

$$F_o \cong 2\Delta T(2\alpha)^{-1/2}\left(\pi\rho_s^3 C_s^3 K_s t_p\right)^{1/4} \qquad (6)$$

where, ΔT is the rise in temperature, α the absorption coefficient, ρ_s the density, C_s the heat capacity, K_s the thermal heat conductivity and t_p is the laser pulse width. Using the value of ΔT from Equation 5 we estimated the value of ablation coefficients at different wavelengths (Table I). Values used in the calculation are $\rho_s = 2.28$ gm/cm^3, $C_s = 3.592$ J gm^{-1} K^{-1} (at 2533 °K), $K_s = 1.484 \times 10^{-2}$ W cm^{-1} K^{-1} (at 2533 °K), $t_p = 8$ nsec and $\Delta T = 2533$ °K. The results are in good agreement with the experimental observations that at lower wavelength the absorption coefficient is much higher than at higher wavelength. The same results follow from Fig. 4; namely, the amplitude of the deflection rises more rapidly at lower wavelength.

4. Conclusion

We have used the photothermal deflection technique successfully to determine the ablation threshold of Teflon at different harmonics of the Nd:YAG laser. It is found that it is a very weakly absorbing polymer in the IR region; its ablation coefficient increases at lower wavelength. The results agree with the theoretical estimates.

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