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Photophysical ablation of organic polymers: the influence of stresses

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Abstract

Non-stationary effects and the influence of mechanical stresses during ns and ps UV excimer laser ablation of organic polymers are discussed. Direct comparison of theoretical calculations with experimental data for laser ablation of polyimide at different wavelengths shows that the photophysical ablation model describes the kinetics of ns UV laser ablation reasonably well. Small gaseous fragments produced within the bulk polymer may be responsible for the mass losses observed near the ablation threshold. At higher fluences, stresses caused by these fragments may facilitate photophysical ablation. With ps laser pulses, acoustic waves related to transient thermal stresses lead to additional defect formation.

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1. Introduction

The mechanisms responsible for the decomposition and ejection of material in polymer ablation are still under discussion [1–4]. While for ns UV excimer laser ablation of polymers like PMMA photochemical (non-thermal) mechanisms seem to be important, the situation is less clear for polyimide (PI).

Purely *photochemical* models do not explain the appearance of an Arrhenius-type dependence of the mass loss on laser fluence Φ observed near the ablation threshold, Φ_{th} , of PI [4].

Purely *thermal* models require either very high temperatures (near Φ_{th} up to $(6-10) \times 10^3$ K [5]) or very low activation energies. For example, for 248 nm radiation the experiments [4] yield $\Delta E \approx 0.7$ eV which is in contradiction with the good thermal stability of PI.

These difficulties have been overcome in our photophysical ablation model which takes into account thermal desorption of electronically *excited* species [6,7]. Along these lines, an interpretation of measured ablation rates requires surface temperatures of only about 2000 K, which is in excellent agreement with direct temperature measurements for PI [3]. The same model also explains the absence of certain types of surface instabilities [8].

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In the present paper we discuss *transient* ablation regimes which are relevant for ns laser pulses. Additionally, we investigate the effect of internal stresses caused by product species generated within the bulk material. The theoretical results will be compared with experimental data on PI.

2. Photophysical ablation

The model employed in this work is a generalization of the one proposed in [6–8] where the absorption and the thermalization of the excitation energy were considered within a two-level system. To take into account bleaching effects observed in PI for KrF-laser radiation [9], and darkening effects observed for 351 and 308 nm radiation [10,11], we consider the *four-level* system shown in Fig. 1. The excitation–relaxation paths consist of the following steps:

Excitation of level N_1 by absorption of a photon $h\nu$; fast relaxation ($\tau_1 \rightarrow 0$) from N_1 to N^* , a transition $N^* \rightarrow N_2$ by absorption of another photon $h\nu$; fast ($\tau_2 \rightarrow 0$) relaxation to N^* . The stationary solution of the kinetic equations for the population of levels yields for the absorption coefficient

$$\alpha = \alpha_0(1 + sq)/(1 + q), \quad q = I\sigma_{01}t_T/h\nu, \quad (1)$$

where $s = \sigma_{12}/\sigma_{01}$, α_0 is the linear absorption coefficient for $q \rightarrow 0$. Thus, absorption decreases with laser intensity if $s < 1$, and increases if $s > 1$.

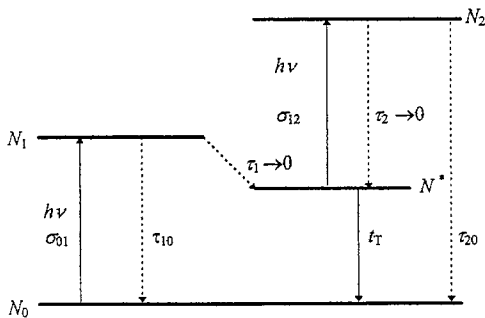


Fig. 1. Schematic picture of electronic energy levels and different channels of energy relaxation. Here, we consider fast ($\tau_1 \rightarrow 0$, $\tau_2 \rightarrow 0$) and slow ($\tau_{10} \gg t_T$, $\tau_{20} \gg t_T$) relaxation processes.

The concentration of excited species N^* , the laser intensity I , and the temperature T , are, in analogy to [6–8], given by

$$\frac{\partial N^*}{\partial t} = v \frac{\partial N^*}{\partial z} + (N - N^*) \frac{I\sigma_{01}}{h\nu} - \frac{N^*}{t_T}, \quad (2)$$

$$\frac{\partial I}{\partial z} = -I\sigma_{01}[N + (s - 1)N^*], \quad (3)$$

$$\frac{\partial T}{\partial t} = v \frac{\partial T}{\partial z} + D_T \frac{\partial^2 T}{\partial z^2} + \left(I\sigma_{01}s + \frac{h\nu}{t_T} \right) \frac{N^*}{\rho c_p}. \quad (4)$$

Here, N is the concentration of chromophores. The ablation velocity is

$$v = v(t) = \left(1 - \frac{N_s^*}{N} \right) v_A \exp(-\Delta E/T_s) + \frac{N_s^*}{N} v_A^* \exp(-\Delta E^*/T_s), \quad (5)$$

where ΔE and ΔE^* are activation energies for ground state and excited species, respectively. The subscript s refers to the ablation front at $z = 0$, i.e., $T_s \equiv T(z = 0)$, etc. The boundary and initial conditions are

$$\kappa \frac{\partial T}{\partial z} \Big|_{z=0} = \rho \left[\left(1 - \frac{N_s^*}{N} \right) v_A \Delta H \exp(-\Delta E/T_s) + \frac{N_s^*}{N} v_A^* \Delta H^* \exp(-\Delta E^*/T_s) \right], \quad (6)$$

$$I|_{z=0} = I_0(t) \exp \left[-\alpha_g \int_0^t v(t_1) dt_1 \right],$$

$$N^*|_{z \rightarrow \infty} = 0, \quad T|_{z \rightarrow \infty} = T_\infty, \quad (7)$$

$$N^*|_{t=0} = 0, \quad T|_{t=0} = T_\infty. \quad (8)$$

Here, $\kappa = D_T c_p \rho$ is the thermal conductivity and D_T the thermal diffusivity. ΔH and ΔH^* are transition enthalpies. The shielding of the laser radiation by the ablated products is taken into account in Eq. (7). α_g is the absorption coefficient within the plume recalculated to the depth of ablated material. $I_0(t)$ describes the temporal shape of the laser-beam intensity.

3. Numerical results

Steady-state ablation (solutions of Eqs. (2)–(7) with constant velocity v_s) was studied in [6]. The

time required to reach steady-state conditions (at constant I_0) can be estimated from $\tau_s = \max(D_T/v_s^2, 1/\alpha v_s)$. In typical experiments, the laser pulse duration is $\tau_1 \leq \tau_s$ and I_0 changes with time. Thus, a quantitative description of laser ablation should include the temporal dependence of the ablation velocity, $v(t)$. Eqs. (2)–(8) were solved numerically using the finite element method [12]. Within physical ranges ΔE , v_A and ΔH did not significantly influence the results. The values of v_A^* , ΔH^* , ΔE^* , t_T , α_g and s were used as fitting parameters to the experimental curves and were varied only within physically admissible ranges. For example, the activation energies derived are in good agreement with representative values of ΔE and ΔE^* for organic molecules [13] and v_A , v_A^* are of the order of the sound velocity in polymers.

Bleaching (darkening) strongly influences the laser ablation kinetics. The transient time required to establish stationary intensity profiles depends on the parameter s and increases when s decreases because of the decrease in the effective α (see Eq. (1)). Thus, the duration of transient ablation depends not only on laser intensity and pulse width, but on the laser wavelength as well.

The ablated thickness per pulse depends on both the total fluence and the temporal shape of the laser pulse. In our calculations we consider a triangular pulse which corresponds to the experiments [4]. The maxima in surface temperature and ablation velocity are reached *after* the maximum in laser intensity. The thermal relaxation time employed was several hundred ps. As a result, the shape of $N_s^*(t)$ is almost similar to the shape of the laser pulse with FWHM $\tau_1 = 15$ ns. The characteristic time for the decrease in surface temperature, $T_s(t)$, is significantly longer than τ_1 .

The calculated ablation rates (in Arrhenius variables $\{\log(\Delta h), 1/\Phi\}$) for different wavelengths are shown in Fig. 2 by the full curves. The linear dependences suggest that the experimental data for low fluences, can be explained by thermal ablation (depletion) mechanisms. If we assume c and D_T to be constants, we derive for $\lambda = 248$ nm an activation energy $\Delta E^* = 1.27$ eV. If the dependences $c(T)$ and $D_T(T)$ are taken into account, then, according to [4], one finds $\Delta E^* = 0.7$ eV. At higher fluences sublimation and bleaching (for $\lambda = 248$ nm) lead to a

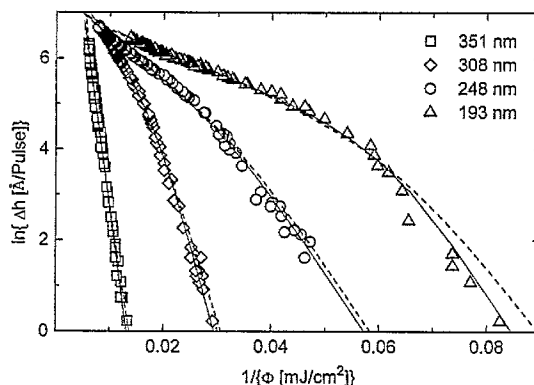


Fig. 2. Kinetic curves in Arrhenius variables $-\log(\Delta h)$ versus $1/\Phi$. Model calculations (parameters are the same as in [14]) are shown by full curves. Dashed curves represent the fit by the interpolation formula $\Phi = B \exp(\alpha_f \Delta h) / \ln(A/\Delta h)$ [7], which takes into account shielding of the laser radiation by the ablated products. The experimental data [4] are also shown.

sublinear dependence of $T_{s \max}$ on Φ . This results in a decrease in the slope (see Fig. 2). Numerical integration of Eqs. (2)–(8) confirms this effect. However, the calculated change in slope is smaller than that observed experimentally [4]. This discrepancy may be due to the absorption of the incident laser radiation by gas-phase ablation products ($\alpha_g \neq 0$). Details of these calculations are given in [14].

The calculated temperatures are significantly smaller than those obtained from a purely thermal model, mainly due to the small activation energy ΔE^* . The maximum temperature, $T_{s \max}$ decreases further when we take into account the temperature dependences of the heat capacity and heat diffusivity.

Photophysical ablation requires relatively long thermal relaxation times. Although these values may be realistic for some organic polymers [15], they are an order of magnitude higher than the decay time found with 355 nm radiation for PI [11].

Another problem related to the temperature rise is the effect of the laser pulse duration onto the ablation kinetics. According to [16] the etch depth is independent of τ_1 , which is in agreement with photochemical ablation. On the other hand, [4] suggests that $T_s = \text{const.}$ at $\Phi = \Phi_{\text{th}}$. It leads to a dependence of $\Phi_{\text{th}} = \Phi_{\text{th}}(\tau_1)$ as shown in Fig. 3. Photophysical ablation predicts an increase of Φ_{th} with τ_1 . Reliable experimental data [1,4,16] are, however, all located

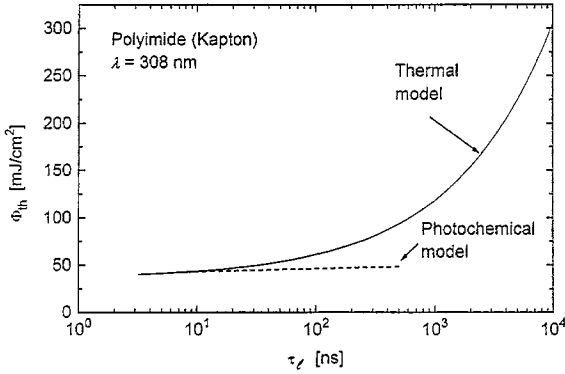


Fig. 3. Dependence of the Φ_{th} on τ_l for 308 nm laser radiation. Full curve: Thermal model for $T_{s,max} = 2300$ K. Calculated from

$$T_{s,max} = T_x + \frac{\Phi_{th}}{\tau_l \kappa} \left\{ \frac{2\sqrt{D_T \tau_l}}{\sqrt{\pi}} - \frac{1}{\alpha_0} \times \left[1 - \exp(-\alpha_0^2 D_T \tau_l) \operatorname{erfc}(\sqrt{\alpha_0^2 D_T \tau_l}) \right] \right\}.$$

Dashed curve: Photochemical model. A rectangular laser pulse and the same constants as in [4] have been employed.

between about 15 and 30 ns, where the predictions of two models are similar.

4. Defect formation within the bulk

Up to now we ignored bond breaking within the bulk. In other words, we assumed that ablation results from decomposition reactions which take place within a very thin surface layer whose thickness is significantly smaller than the absorption depth α^{-1} . Now, we take into account decomposition reactions within the bulk. These can again be thermally or/and photochemically activated. The effect of photochemical modification on the ablation kinetics was studied in [17]. Here, we consider *thermally* activated reactions. In any case a self-consistent theoretical treatment requires the consideration of stresses which are induced within the polymer. The activation energies for both defect formation and (surface) ablation (Eq. (5)) can be described by [18]

$$\begin{aligned} \Delta E(\sigma) &= \Delta E_0 - \gamma\sigma, \\ \Delta E^*(\sigma) &= \Delta E_0^* - \gamma^*\sigma, \end{aligned} \quad (10)$$

where σ denotes the stress.

Let us assume that bond breaking results in the formation of two types of defects: ‘Heavy’ fragments that include one or more monomers, and ‘light’ fragments, consisting of simple molecules like CO, CN, CH₂, etc. Any related changes in the physical properties of the bulk material will, at present, be ignored. For the number density of light fragments, N_1 , the diffusion equation can be written as

$$\frac{\partial N_1}{\partial t} = v \frac{\partial N_1}{\partial z} + \frac{\partial}{\partial z} \left(D_1 \frac{\partial N_1}{\partial z} \right) + Q_1. \quad (11)$$

The source term Q_1 is given by

$$\begin{aligned} Q_1 = (N_{01} - N_1) & \left(\eta_1 \frac{\sigma_{01} I}{h\nu} + k_1 \exp \left[-\frac{\Delta E_1}{k_B T} \right] \right. \\ & \left. + k_1^* \exp \left[-\frac{\Delta E_1^*}{k_B T} \right] \right), \end{aligned} \quad (12)$$

where k_1 , k_1^* depend both on N^* , and $\Delta E_1 \equiv \Delta E_1(\sigma_{zz})$, $\Delta E_1^* \equiv \Delta E_1^*(\sigma_{zz})$. The first term describes the generation of light species by *direct* photochemical bond breaking with quantum yield η_1 . The second and third term describe the thermomechanical generation of such species from ground state and excited molecules, respectively. Q_1 vanishes when $N_1 \approx N_{01}$. The effect of stresses on electronically excited species exceeds that of ground state species, because $\Delta E_0^* < \Delta E_0$ and $\gamma^* > \gamma$ [13]. In polymers, γ can have values up to 10^{-21} cm³ (for PMMA $\gamma = 1.7 \times 10^{-21}$ cm³ [18]).

The light fragments may be treated as an ideal gas which cause an average pressure $p = \zeta N_1 k_B T$ with $\zeta < 1$ (only a fraction of the total number of these species will contribute to p). The diffusion coefficient D_1 depends on pressure p [19] and temperature T . When the light species reach the surface $z = 0$, they desorb and cause a mass loss [20]. When real ablation can be ignored, the flux of species which desorb from the surface and the corresponding mass loss per unit area can be approximated by

$$-J_1 \equiv D_1 \frac{\partial N_1}{\partial z} \Big|_{z=0} = \beta N_1 \Big|_{z=0} \quad \text{and} \quad \frac{dM_1}{dt} = -m_1 J_1, \quad (13)$$

where $\beta \equiv \beta(T)$ describes the properties of the polymer surface, and m_1 the average mass of light fragments. The second boundary condition is

$$N_1|_{z=\infty} = 0. \quad (14)$$

Real surface ablation takes place for $\Phi > \Phi_{th}$. The velocity of the ablation front is given by Eq. (5). In a *generalized* formula the preexponential factors in Eq. (5) may depend on the surface concentration of broken bonds and on *modified activation energies* as in Eq. (10). Note that $\sigma_{zz}(z=0)$ and $N_1(z=0)$ are *not* equal to zero, and thereby influence the ablation process. The *total* mass removal (per unit area) is given by the sum of surface and volume processes

$$\Delta M = \Delta M_a + \Delta M_1 = \rho \int_0^\infty v(t) dt + \int \frac{dM_1}{dt} dt. \quad (15)$$

The second term is important only when real ablation can be ignored, otherwise light species are removed together with the bulk material. Near and below Φ_{th} mass removal due to light fragments can be comparable or even exceed mass removal due to real ablation.

To make the problem self-consistent we must employ also the equation of thermoelasticity [21]

$$\frac{\partial^2 \sigma_{zz}}{\partial t^2} = c_s^2 \frac{\partial^2 (\sigma_{zz} - p)}{\partial z^2} - \frac{E_Y}{3(1-2\mu)} \frac{\partial^2}{\partial t^2} [\alpha_v(T - T_0)]. \quad (16)$$

Here α_v is the volume thermal expansion coefficient, E_Y Young's modulus, μ the Poisson ratio, and c_s is the sound velocity. Eq. (16) should be solved together with the boundary conditions

$$\sigma_{zz}(t, z=0) = p(t, z=0), \quad \sigma_{zz}(t, z=\infty) = 0. \quad (17)$$

The set of equations which describe the ablation process consists now of Eqs. (2)–(8), and (10)–(17). Here, any bulk transformation (amorphization, melting) and reaction enthalpies should be included in Eq. (4). In principle, 'heavy' fragments produced within the bulk may also induce stresses due to changes in the specific volume, and their influence

should be included in Eq. (16) as well. Let us discuss two limiting cases:

For laser pulse lengths $\tau_1 \gg 1/\alpha c_s$, the stresses are due to the hydrostatic pressure caused by the light fragments, $\sigma = p$. Then we obtain from Eqs. (2)–(8), and (10)–(14) that the effect of stresses changes the preexponential factors in Eq. (5) and correspondingly influences the mass removal described by Eq. (15). The characteristic scaling factors $\exp[\gamma N_1]$ and $\exp[\gamma^* N_1]$ are of the order 1 to 10^2 , depending on the mechanism of defect formation.

The stresses caused by the light species may be especially important for 193 nm radiation where the photophysical model requires an unreasonably big value of v_A^* in Eq. (5) [14]. It can also modify some fitting parameters for other wavelengths. For a detailed analysis one has to measure the two terms in Eq. (15) separately.

5. Transient stresses

For very short laser pulses, the effect of stresses becomes even more pronounced. If $\tau_1 \leq 1/\alpha c_s$, we should take into account also transient stresses which result in the formation of intense acoustic waves [22]. Here, we consider only thermal stresses in Eq. (16) and set $p = 0$. We also ignore the photogeneration of defects (first term in Eq. (12)), diffusion, and

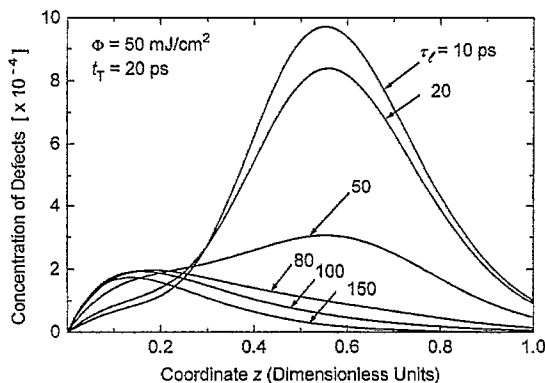


Fig. 4. Spatial distribution of defects generated by acoustic waves related to transient thermal stresses. Thermal relaxation time $\tau_T = 20$ ps. The number density of defects is normalized to the total number density of chromophores. The coordinate is given in units $1/\alpha$. Parameters are the same as in [22].

the motion of the ablation front ($v = 0$ in Eq. (11)) near Φ_{th} . Finally, we assume that both compressive and tensile stresses *decrease* activation energies and use $|\sigma_{z,z}|$ in Eq. (10) (compressive stresses may decrease ΔE due to local plastic deformations [23]). The result of these calculations is shown in Fig. 4 for various values of τ_1 and $t_T = 20$ ps. A decrease in pulse duration increases the number of defects.

Defect generation is determined by the concentration of excited species, the temperature, and mechanical stresses. It leads to a non-monotonous dependence of the maximum value of generated defects on pulse duration when $t_T \geq 1/\alpha c_s$. At moderate fluences, a single maximum related to tensile stresses appears.

Irreversible changes in material properties lead to an accumulation of defects for multi-pulse irradiation.

6. Conclusion

The experimental data [3,4] from excimer-laser ablation of PI can be explained on the basis of transient photophysical ablation which takes into account changes in absorption due to bleaching and darkening effects. The model permits to explain the following experimental results:

- Arrhenius-like kinetic curves for fluences $\Phi < \Phi_{th}$.
- Activation energies considerably smaller than bond breaking energies.
- Fairly high ablation rate at relatively low surface temperature.
- The absence of certain types of surface instabilities [8].

We predict that the threshold fluence increases with pulse length, in contrast to [16]. We also predict that stresses, caused by light fragments, strongly influence the ablation rate.

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