Theory of polymer ablation
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Citation: Appl. Phys. Lett. 53, 2377 (1988); doi: 10.1063/1.100235
View online: http://dx.doi.org/10.1063/1.100235
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The light pulses from short-wavelength excimer lasers have been shown to etch clean holes in polymers.\textsuperscript{1,2} This process has numerous applications in medicine and in the manufacture of integrated circuits.\textsuperscript{3-4} Here we examine the theory of this process, and derive a new and simple formula for the etch depth \( l \) per pulse for a laser of fluence \( F \).

Experiments have shown that the ablation process is not just due to local heating, but involves some other process which presumably is bond breaking. Define \( n(x,t) \) as the number of broken bonds per unit volume at a position \( x \) from the surface at the time \( t \). We follow previous theories in assuming that ablation occurs whenever this bond breaking density exceeds some threshold value \( n_l \).\textsuperscript{5-8}

The first laser pulse produces a damage profile given by Beer's law of \( n = (f a F / h \nu) \exp(-\alpha x) \), where \( \alpha \) is the absorption coefficient, \( h \nu \) is the photon energy, and \( f \) is the fraction of absorbed photons which break bonds.

\[
l = (1/\alpha) \int \left[ F / F_l \right] \theta(F - F_l),
\]

where \( \theta \) is the step function. This formula has been widely used to interpret ablation data.\textsuperscript{6,9-11} The initial experiments seemed to show that \( l \) is proportional to \( \ln(F) \), although the range of values for \( F \) was small. Recent experimental plots for large ranges of \( F \) show that Eq. (1) is not obeyed.\textsuperscript{7,12}

Experimental data are usually taken by averaging over many laser pulses. A key aspect of our theory is that broken bonds remain in the unetched portion of the polymer. The exponential nature of Beer's law guarantees that substantial bond breaking density remains in that part of the polymer which is not etched away. The next laser pulse builds on this residual bond breaking density. Equation (1) is only valid for the first laser pulse, but is invalid for subsequent pulses since it ignores the residual bond breaking. This model distinguishes bond breaking from purely thermal effects. The low repetition rate of the pulses, on the order of Hertz, means that heating effects will dissipate between pulses.\textsuperscript{13,14}

However, the bond breaking which turns a polymer into a monomer seems to have a much longer relaxation time. Since the density of broken bonds is low, we can assume that their presence does not change physical parameters such as the absorption coefficient.

Ample evidence exists for the concept of residual bond breaking density. For polymers of low absorption coefficient, numerous laser pulses must be absorbed before any ablation occurs.\textsuperscript{7} This makes sense if the polymer is accumulating residual broken bonds from each pulse. We introduce the concept of incremental ablation depth. It is the etch depth per laser pulse \( l \) after many pulses; that is, after the threshold processes are over and actual ablation occurs. We show below that incremental ablation has \( l \) proportional to \( F \) rather than to \( \ln(F) \).

Our theory also employs the concept of a moving melt front as introduced by Keyes \textit{et al.}\textsuperscript{15} Typical laser pulses have a duration of 5–10 ns, during which time the ablated monomer can travel many microns away from the surface. We assume that the ablated material leaves the light path of the laser and no longer causes absorption. Let \( s(t) \) be the position of the polymer surface during a single laser pulse. If the period of the laser repetition is \( 2t_r \), then we consider a single pulse during the duration \( (-t_r,t_r) \) where the pulse is a maximum at the surface at time \( t=0 \). The distance marker \( x \) is defined in a fixed reference frame from where the surface is at the start of a laser pulse. The distance from the actual surface is \( x - s \). The rate at which bond breaking occurs is

\[
\frac{dn(x,t)}{dt} = \frac{f a F}{h \nu} \exp\left(-\alpha[x - s(t)]\right),
\]

where the laser intensity \( I (3/\text{cm}^2 \text{s}) \) is defined in terms of the fluence \( F (3/\text{cm}^2) \) and the normalized pulse shape \( i(t) \):

\[
I(t) = Fi(t),
\]

\[
1 = \int_{-t_r}^{t_r} dt' i(t').
\]

Equation (2) is solved by direct integration. The residual density of broken bonds \( n_l \exp(-\alpha x) \) is taken as the initial condition

\[
n(x,0) = \frac{f a F}{h \nu} e^{-\alpha x} \int_{-t_r}^{t_r} dt_i(t) e^{\alpha x(t)} + n_l e^{-\alpha x}.
\]

The position of the ablation surface \( s(t) \) is defined by setting \( n(s,t) = n_l \) in Eq. (4). Then multiplying each term by the factor of \( \exp(\alpha x)/n_l \) gives the equation for \( s(t) \):

\[
J(t) = e^{\alpha s} = 1 + \lambda \int_{-t_r}^{t_r} dt_i(t_j) J(t_j),
\]

\[
\lambda = \frac{f a F}{h \nu n_l}.
\]

We differentiate this equation with respect to time, which immediately brings us to the equation:

\[
\frac{dJ(t)}{dt} = \lambda i(t) J(t),
\]


FIG. 1. Etch depth $l$ vs laser fluence $F$ for three different polymers. The polyimide (PI) data are from Ref. 7 while the polymethylmethacrylate (PMMA) and poly($\alpha$-methyl) styrene (PS) data are from Ref. 12.

Our new formula (Eq. (5)) is valid over most of the range in values for fluence. At very large values of fluence one gets into the plasma regime, where the polymers become ionized and the etch depth no longer increases linearly. Also, at very low fluence ($F < 0.1\text{cm}^{-2}$) sometimes one finds that no ablation occurs regardless of how many pulses are incident, and there is a slight dependence upon pulse duration.\(^\text{17}\)

Obviously our theory needs refinement in order to account for these two extremes of experimental parameters. Perhaps some annealing of bond damage can occur between laser pulses. Nevertheless, the theory works well over the range of values which have been reported in most experiments.

The theory can also be used to model the thermal behavior during the ablation process. We assume that the fraction $(1 - f)$ of the absorbed photon energy produces heat. The residual heat dissipates away between laser pulses if the repetition rate is less than 50 Hz.\(^\text{14}\) If $C$ is the heat capacity, from Eq. (4) we deduce that the temperature increase during the heat pulse is given by

$$\Delta T(x,t) = (1 - f) \frac{\alpha F}{C} e^{-\alpha s} \int_{-t}^{t} dt \, i(t)e^{\alpha s}.$$  

Using Eq. (4) we can rewrite this as

$$\Delta T(x,t) = \left[ (1 - f) \frac{\alpha F}{C} \right] \left[ n(x,t) - n_T e^{-\alpha s} \right] \theta(x - s).$$  

At the end of the laser pulse we replace $n(x,t)$ by $n_T \exp[-\alpha(x - l)]$ and $s$ by $l$. The total heat $\Delta H$ energy remaining in the unablated portions of the polymer is found by integrating this expression over $dx$ from $l$ to infinity which gives

$$\Delta H = (AC/\alpha)\Delta T(l) = (1 - f)AF_T(1 - e^{-F/F_T}).$$  

FIG. 2. Etch depth $l$ per pulse vs the absorption coefficient $\alpha$ at the laser frequency. The data show little dependence upon absorption coefficient; the latter span three decades of values. All points measured for the same fluence.
This expression also agrees with the experiments. Figure 3 shows how this theory fits the data of Dyer and Sidhu\(^{13}\) where the voltage reading of the thermocouple indicates the stored energy after ablation. The fit has no adjustable parameters since we used the values of \( F_T = 36 \text{ mJ/cm}^2 \) and \( A = 0.0235 \text{ cm}^2 \) which they suggest. They point out correctly that the stored energy saturates at high fluence because the ablated material carries away the additional heat. From their analysis of the data we deduce the fraction \( f = 0.1 \).

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