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Dynamics of Excimer Laser Ablation of Polyimide Determined by Time-Resolved Reflectivity

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Abstract. The time-dependent intensity profile of pulsed KrF excimer laser radiation reflected from polyimide is determined over a range of laser fluences, from well below to above the ablation threshold. The reflected laser beam is truncated once the incident laser radiation exceeds a threshold fluence, i.e., truncation depends on the energy per unit area and not on the intensity, analogous to results for the ablation threshold and the etch depth per pulse. The threshold fluence for pulse truncation corresponds to the onset of ablation. The results indicate that the truncation is not due to laser plasma interactions at these fluences. A general mechanism is discussed involving a time dependent index of refraction.

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The dynamics of laser ablation of polymers has received attention in theoretical models recently. The concept of a moving front [1], the rapid onset of ablation [2], and an intensity dependent absorption coefficient [3] are recent significant contributions to the theory of laser ablation which have received some experimental verification. For example, verification of the existence of a moving ablation front and rapid onset of ablation was provided by the photoacoustic experiments of Dyer and Srinivasan [4], which indicated that the onset of ablation was about 2–4 ns from the rising edge of laser pulses which were tens of nanoseconds wide. The optical experiments of Meyer et al. [5] led to the same conclusion for the 193 nm ablation of polystyrene. The photoacoustic, reflection, and luminescent emission work of Chuang and Tam [6] indicated that there was interaction of the laser beam with the ablation products even for a short 30 ps pulse of a KrF laser. Very recently, the high speed imaging experiments of Simon [7] have more directly shown that ablation occurs during the laser pulse. On the other hand, the idea of an intensity dependent absorption coefficient has been used to interpret the different behavior of plots of etch depth per pulse vs. fluence for femtosecond and nanosecond wide pulses [3].

There have been relatively few experiments reported which explore other aspects of the dynamics of the ablation process, however. Most common has been the determination of the time scale for ejection of ablation products and their internal energies. Taylor et al. [8] have shown that the ablation thresholds and etch depths per pulse for polyimide are virtually the same for 7 ns and 300 ns XeCl laser pulses. The imaging experiments of Kim et al. [9] demonstrated a self-focussing effect in the 532 nm laser ablation of polymethylmethacrylate due to a transient change in the refractive index, the onset of which depended on fluence, not intensity. Also, Klopotek et al. [10] presented a qualitative description of the shortening of XeCl excimer laser pulses by reflecting the beam off a sheet of polyimide, an effect which was attributed to shielding of the latter part of the laser pulse by a "plasma" produced in the initial part of the pulse.

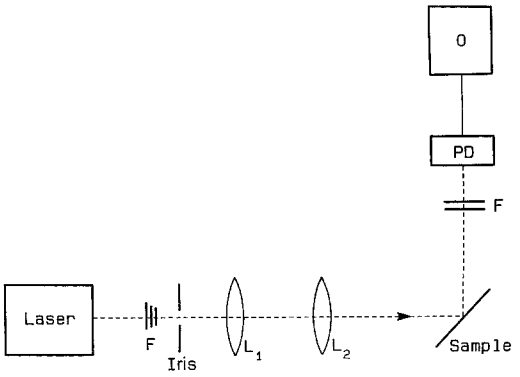

Fig. 1. Schematic diagram of the experiment. F, filters; L_1, 15 cm focal length lens; L_2, 5 cm focal length lens; PD, photodiode; O, oscilloscope

Time-resolved reflectivity measurements were also reported by Dijkkamp et al. [11] for a very different system designed to show that a thermal ablation mechanism could occur for certain polymers.

We describe here the results of quantitative studies of the fluence dependence of the width of the reflected KrF excimer laser pulse from polyimide, below and above the threshold for ablation, and discuss the implications of the results on the mechanism for ablation. The results emphasize the importance of the processes occurring from the start of the laser pulse to the onset of ablation.

The experimental arrangement is shown in Fig. 1. Polyimide foil (Kapton-H), 135 μm thick, was etched with a uniform beam Lumonics HyperEX 460 excimer laser operating at the KrF wavelength (248 nm) with a nominal optical pulse width at half maximum of 20 ns in these experiments. A 5 mm diameter iris was used to select a portion of the central, uniform region of the beam, and the diameter of the beam was then reduced by a factor of 3 with a telescope consisting of 15 cm and 5 cm focal length lenses. Because the polyimide was placed at an angle of 45° with respect to the laser beam, the larger depth of field provided by the telescoping arrangement resulted in a more uniform fluence across the face of the etched zone than could be accomplished by simply imaging an iris onto the target. The incident laser fluence was varied by inserting calibrated optical filters in the beam in front of the iris. Fluence was calculated from the area of the elliptical etched zone and the energy of the laser pulse measured with a Scientech calorimeter, and taking into account the transmission efficiencies of the filters and lenses.

The specularly reflected light was attenuated with optical filters or with an interference filter centered at 249 nm and detected with a fast photodiode (ITLTF1850) and oscilloscope (either a Tektronix 7834 with 7A19 amplifier and 7B92A plug-in units or a Tektronix 466). The oscilloscope trace was photographed and enlarged for measurement of the pulse width and of the relative values of the fluence. The latter were obtained as the area under the signal trace measured with a planimeter. The linearity of the detection system was verified by plotting the reflected peak intensity from a fused quartz plate as a function of the incident fluence.

In a separate set of experiments, it was found that at very low fluences neither the peak intensity nor the pulse width of the reflected beam changed with successive laser pulses on the same spot of the polyimide, even for as many as 300 pulses. However, above about 20 mJ/cm^2, the peak intensity began to drop with repeated exposure. At fluences of 22, 37, and 59 mJ/cm^2, the peak intensity on the 300th pulse was 85%, 10%, and 8% of the value of the first pulse. However, as the fluence increased further, the peak intensity of the 300th pulse began to approach that of the first pulse, for example, 63% at 190 mJ/cm^2. These results can be interpreted in terms of cone formation at fluences near threshold [12], which serve as light traps and prevent reflection of the beam. At higher fluences, cones are not formed, and a smooth reflective surface is left after each pulse.

Below about 20 mJ/cm^2, the reflected pulse from polyimide has the same temporal profile as the pulse reflected from a thin fused quartz plate. With increasing fluence, however, the reflected pulse width decreases, as shown in Fig. 2 for four fluences. Although the pulse width does not vary significantly for the first hundred pulses or so, the intensity does, and each trace in Fig. 2 was obtained on a fresh surface. It is evident in

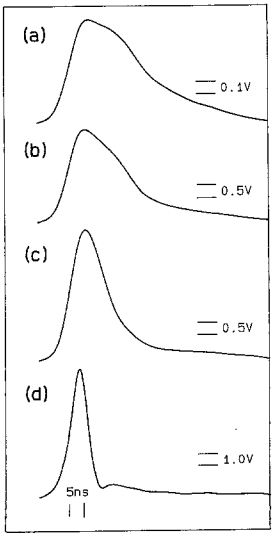

Fig. 2. Traces of the 248 nm laser pulse reflected from polyimide at several fluences. (*a*) 9.4 mJ/cm^2; (*b*) 32 mJ/cm^2; (*c*) 48 mJ/cm^2; (*d*) 150 mJ/cm^2

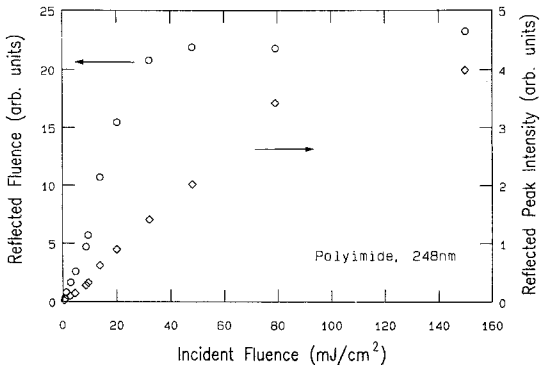

Fig. 3. Plots of the reflected fluence (○) and reflected intensity (◇) as a function of fluence of a 248 nm laser pulse incident on polyimide

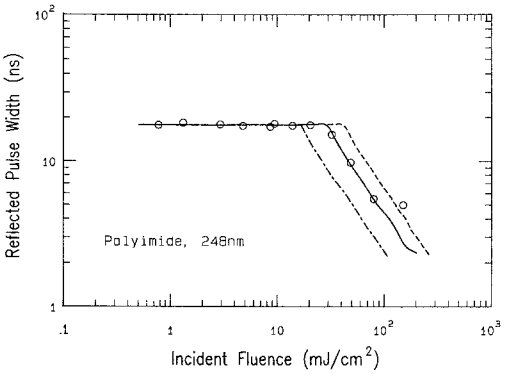

Fig. 4. Plot of the full width at half maximum of the 248 nm laser pulse reflected from polyimide as a function of incident laser fluence. The lines are calculated for threshold fluences of 13 mJ/cm² (– · –), 23 mJ/cm² (——), and 33 mJ/cm² (– –), as described in the text

the figures that for incident fluences up to about 100 mJ/cm², the reflected pulse is truncated on the trailing edge, and not the rising edge. This is shown more quantitatively in Fig. 3, where the peak intensity of the reflected pulse increases linearly with increasing incident fluence up to at least ~100 mJ/cm². Thus, the process responsible for clipping the trailing end of the laser pulse is not suddenly switched on once a threshold intensity is reached. On the other hand, the fluence of the reflected laser pulse is essentially constant once the incident laser fluence exceeds the threshold value, as seen in Fig. 3, where the fluence of the reflected pulse is given in arbitrary units. Specifically, over a 7-fold change in incident fluence (from 20 to 150 mJ/cm²), the reflected fluence is within 30% of the average value. This is a significant finding, in that it shows that on the time scale of the experiments, the process responsible for decreasing the reflectivity of polyimide involves a fluence threshold, and not an intensity threshold.

The experimentally observed pulse widths in Fig. 2 can be reasonably reproduced, to within about 1 ns, if we assume that reflection ceases abruptly after an incident fluence of 23 mJ/cm² is reached. The comparison of the calculated and experimental reflected peak widths at half maximum intensity is made in Fig. 4. In the calculations, the laser pulse reflected from polyimide at low fluences is taken as the shape of the incident laser pulse. The threshold value of 23 mJ/cm² was selected as a reasonable fit to the data. The sensitivity of the calculated results to the threshold fluence is indicated by the broken lines in Fig. 4, which were calculated for threshold values of 13 and 33 mJ/cm². Also, the fitted lines are sensitive to the shape of the incident laser pulse. The calculated width of the reflected pulse at half maximum does not decrease until the total fluence of the incident pulse exceeds the adopted threshold value by about 30% (for the pulse shape in these experiments), because it is not until the trailing edge is clipped at an intensity higher than the half maximum intensity that the peak width at half maximum will be altered. Also, at very high fluences, the calculated reflected pulse width is sensitive to the steepness of the rising edge of the pulse. The calculated pulse width does not decrease indefinitely with increasing fluence because of the slow rise time at the very onset of the laser pulse. Thus there is an optimum fluence for obtaining the minimum pulse width, which is a consideration if this technique were to be used as a method for generating short excimer laser pulses, as proposed by Klopotek et al. [10].

Although the threshold value of 23 mJ/cm² used in the calculations is an approximation, it is suggestively close to the experimentally determined ablation threshold of 17 mJ/cm², obtained using a photoacoustic method described previously [8]. The photoacoustic threshold corresponds to the onset of ejection of gaseous products, which must also account for the onset of the truncation of the reflected beam at about this fluence. One feature of the reflected pulse shapes in Fig. 2c and d which is not reproduced by this simple model is the long sloping tail following the sudden drop in reflected intensity. This feature indicates that the reflectivity does not drop completely to zero.

Klopotek et al. [10] suggested that the clipping of the reflected laser pulse is caused by formation of a plasma during the ablation process which absorbs the trailing part of the pulse. However, it is unlikely that a plasma forms at the low laser fluences at the onset of the clipping of the laser pulse (~30 mJ/cm², corresponding to a peak intensity of ~2 MW/cm²). Experimental evidence for the extent of plasma formation in laser ablation of polyimide is inconclusive. At considerably higher fluences up to 5 J/cm², Walkup et al. [13] concluded that there was no significant plasma

(degree of ionization of ~0.1–1.0%) in the 248 nm laser ablation of polyimide and polymethylmethacrylate, as probed by interferometry. However, it is likely that any plasma initially formed would have significantly decayed via electron–ion and ion–ion recombination by the time the plume reached the detection zone in their interferometric experiments [13]. Optical emission studies give only qualitative evidence of ionized species at high fluences [14].

An alternative mechanism which may explain the time dependence of the reflected intensity involves a transient change in the reflectivity of the polyimide-air interface. For simplicity, we consider the case of normal dispersion and normal incidence of the radiation, for which the reflectivity, R, of an absorbing substrate is given by [15]

$$R=(\mathbf{n}-\mathbf{n}')(\mathbf{n}^*-\mathbf{n}'^*)/(\mathbf{n}+\mathbf{n}')(\mathbf{n}^*+\mathbf{n}'^*)$$

where $\mathbf{n}$ and $\mathbf{n}'$ are the complex indexes of refraction of polyimide and of air, and $\mathbf{n}^*$, $\mathbf{n}'^*$ are their complex conjugates. Each complex index of refraction is given by $\mathbf{n}=n(1-ix)$ where n is the real part of the index and x is the attenuation coefficient. In order for R to decrease to near zero, the complex index of refraction of polyimide and of air must approach each other. Just prior to ejection of material from the surface, the index of refraction of photochemically modified polyimide could approach that of air. However, the process is very complex, and both real and imaginary parts of the index of refraction may play roles, each with its own time dependence.

As the results in Fig. 3 show, the decrease in reflectivity, and hence the modification of the index of refraction of the polyimide surface, is evidently not dependent on the incident laser pulse reaching a critical intensity, but rather on its reaching a critical fluence, estimated in the above discussion as ~23 mJ/cm^2. A very similar result has been reported recently for the time-dependent index of refraction of polymethylmethacrylate (PMMA) induced with a 93 ps laser pulse at 532 nm [9]. Fast imaging of the ablation process indicated transient self-focussing in PMMA, with a duration of about 20 ps just prior to the ejection of ablation products. The onset of self-focussing was induced by the incident laser radiation reaching a critical fluence, not a critical intensity. The results were interpreted in terms of the relaxation time of the laser induced change of the index of refraction. An "intensity threshold" would be expected if the relaxation time were less than the length of the laser pulse, and a "fluence threshold" if it were longer. Similar conclusions can be drawn from the present results. In our case, however, the time scale of the laser pulse is 2 orders of magnitude longer. Although we cannot identify the relaxation time of the transients responsible for alteration of the reflectivity in our work, it is evidently shorter than the time between laser pulses (on the order of a second) since the reflectivity is largely recovered on the subsequent pulse (although it can decrease significantly for other reasons after hundreds of pulses, as described above). The similarity in the results of our present work and that of Kim et al. [9] is all the more remarkable in that PMMA is transparent to 532 nm radiation in contrast to the highly absorbing polyimide at 248 nm in our work.

It is significant that a number of phenomena related to laser ablation of polyimide are dependent on the fluence and not on the instantaneous laser intensity: the clipping of the reflected 248 nm laser pulse observed in the present work, the onset of 308 nm laser ablation [8], and the etch depth per pulse at 308 nm [8]. The similarity of these results emphasizes the importance of fluence, rather than intensity, for ablation of organic materials using pulse widths of tens to hundreds of nanoseconds. It appears therefore that the relaxation rates of the transient properties responsible for these effects (reflection, ablation threshold, etch depth) are quite long and probably very similar. The similarity of the magnitude of the thresholds for ablation and for modification of the reflectivity indicate that the physical processes underlying these observations are probably closely related. While reflectivity offers another way to probe the dynamics of the ablation process, a fuller description of the process would require time-dependent reflectivity data at different wavelengths and polarizations.

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