Schlieren measurements of the hydrodynamics of excimer laser ablation of polymers in atmospheric pressure gas

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Pulsed schlieren photography and fast helium-neon laser deflection are used to study the hydrodynamics of laser ablation of polyethyleneterephthalate and polymethylmethacrylate by pulsed KrF (248 nm) radiation in atmospheric air, Ar and N_2. Schlieren measurements show the evolution of shock waves, sound waves, and reduced-density, hot gas plumes. A transition from sound to shock at the ablation threshold for both polymers is observed. The shock velocity of PET tends to approach agreement with blast wave theory at fluences higher than 1 J/cm^2. Plumes in air are consistently larger than those produced in Ar and N_2 (at fluences below 5 J/cm^2) suggesting that combustion may occur. Laser deflection measurements for PET at 150 mJ/cm^2 indicate a plume density of 0.6 kg/m^3 (50% atmospheric density).

I. INTRODUCTION

Excimer laser ablation is increasingly important in etching of polymeric photoresist in microelectronics and ablative material deposition of thin films. Pulsed ultraviolet photoablation of polymers in gases drives sound and shock waves into both the target and the gas. These acoustic[1] and stress waves[2] can be used as a diagnostic for the determination of the onset of ablation. The generation of sound and shock waves in solids and liquids has also been investigated.[3] Recently, experiments have been reported in which the early time evolution ($t = 0$–60 μs) of excimer laser ablation of polymethylmethacrylate (PMMA) was studied by a probe laser and camera.[4,5] Our work complements that of Refs. 4 and 5 by using schlieren diagnostics to study hydrodynamics on much longer time scales. Previously laser beam deflection (quantitative schlieren) has been used to observe thermal and sound waves generated near the ablation threshold.[1] Laser deflection provides the line averaged density gradient in a gas as a function of time at a particular position parallel to the target. Pulsed schlieren photography has the advantage that it is sensitive to density gradients but provides hydrodynamic information in two dimensions at a particular time, showing clearly such features as shock waves, hot gas plumes, turbulence, or asymmetry in the flows. In this paper both schlieren photography and laser deflection are used to characterize the hydrodynamics of laser ablation of polyethyleneterephthalate (PET) and PMMA in atmospheric pressure gases. The schlieren photographs are the first to show hot, reduced-density plumes in gases which persist up to several ms after the laser ablation pulse.

II. EXPERIMENTAL CONFIGURATION

The ablation source was a beam of pulsed 248-nm radiation from a KrF excimer laser with a maximum energy of 1.5 J/pulse. The excimer laser beam was incident perpendicular to the target surface. Unfocused, the maximum fluence was 200 mJ/cm^2, apertured to approximately 0.7 cm^2. Focused, the fluence could be increased to 10 J/cm^2. For fluences less than 200 mJ/cm^2, the fluence was determined by splitting part of the ablating beam and measuring its energy on a calorimeter and by measuring the burn pattern on a sample of PET. At higher fluences, the fluence was determined by focusing the beam through a pinhole of known diameter and measuring the transmitted energy on a calorimeter. Fluence was varied by inserting quartz plates in the path of the ablating beam.

Schlieren photographs[6] were obtained with 20-ns pulses from an excimer-pumped dye laser system. The dye laser beam was oriented parallel to the target surface, providing a side-on view of the ablation hydrodynamics. The maximum field of view in the schlieren photographs is 5.75 cm. To obtain two-dimensional resolution, the schlieren system utilized a pinhole as in Ref. 7. Simultaneous laser deflection and schlieren measurements were performed by passing a cw HeNe laser beam parallel to the target but oblique to the collimated dye laser beam. The unfocused HeNe beam (probe beam) traveled 0.7 cm across the excimer laser spot; the probe beam was typically greater than 3 mm from the surface, and was incident on a fast position sensitive detector.[8] (In our earlier work,[1] the probe beam was 175–300 μm above the surface.) The rise time of this detector was less than 25 ns. For these experiments the detector was 1.55 m from the sample.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows schlieren photographs of an ablation generated shock and ablation plumes as they evolve in time. Laser energy deposition on the surface ejects material, heats the adjacent gas, and creates a high-temperature plume. The plume is initially attached to the surface but detaches up to approximately 0.7–1 ms (the exact time of detachment varies with fluence). The plume acts like a piston and drives an

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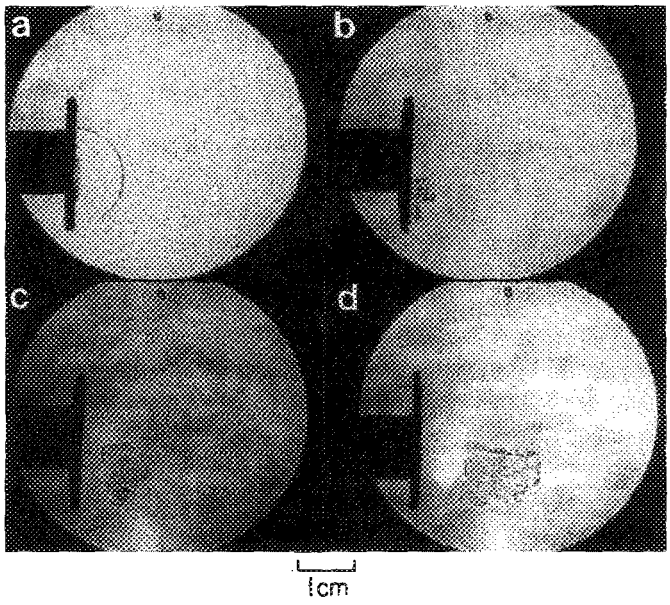

FIG. 1. Schlieren photographs of a plume and shock wave generated by the ablation of PET in air by 248-nm KrF laser radiation. The excimer laser beam was incident from the right of the photo, perpendicular to the target surface. The delay between the dye laser pulse (schlieren) and the excimer laser ablating source was (a) 18 μs, (b) 150 μs, (c) 800 μs, and (d) 2 ms. The fluences are in the range of 140–200 mJ/cm^2.

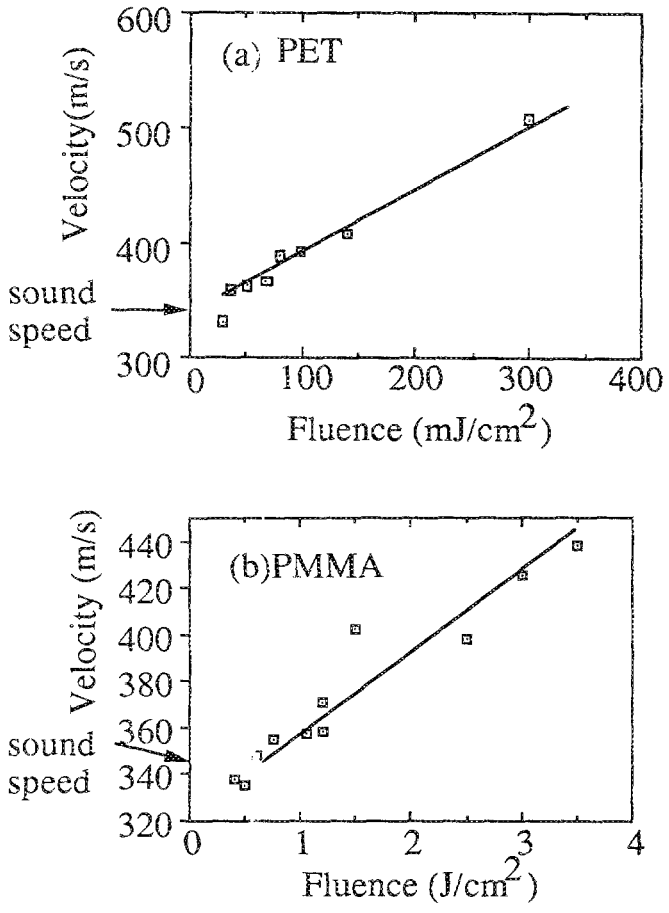

FIG. 2. (a) The sound and shock wave velocities for ablation of PET and (b) PMMA at near threshold fluences in atmospheric air by 248-nm radiation. Each velocity is a local measurement obtained by plotting shock positions vs time and taking the slope. These velocities were constant over the 5-cm schlieren field of view. Each data point corresponds to 5–10 schlieren photographs.

intense sound or shock wave. Shocks are observable for approximately the first 20 μs after the ablating pulse. For low fluences, <300 mJ/cm^2, the velocity of the intense sound/shock waves are constant over the field of view. The plume is observable for the following few ms, during which it becomes turbulent.

Figure 2 shows a plot of the observed shock and sound wave velocities versus fluence for PET and PMMA. It is shown in Fig. 2(a) that there is a transition from a sound wave to a shock wave at the ablation threshold, 20–30 mJ/cm^2 for PET.[1] Between 30 and 300 mJ/cm^2, the velocity increases linearly at 0.6 (m/s)/(mJ/cm^2). Figure 2(b) displays the sound-to-shock transition for PMMA at 500–600 mJ/cm^2. The ablation threshold[9] for significant etching of PMMA occurs at approximately 650 mJ/cm^2. In the fluence range of 600–3500 mJ/cm^2, the shock wave velocity for PMMA increases linearly at 0.035 (m/s)/(mJ/cm^2).

Figure 3 shows the plume leading and trailing edge position as a function of time for a fluence of 100–150 mJ/cm^2. At times less than 1 ms the plume is attached to the surface. Measurements at 100 mJ/cm^2 and 10 J/cm^2 indicate the same power-law dependence for the plume position: x is proportional to $t^{0.5}$. In the 100–150 mJ/cm^2 range, the average plume velocity is approximately 33 m/s.

Our experimental results for plume expansions before they detach from the surface are consistent with previous experiments by Raleigh[10] and Koren.[11] Raleigh's experiments showed that ohmically heated reduced density channels, after attaining pressure equilibrium, grew because of turbulent mixing with x proportional to $t^{0.5}$. Koren ablated polyimide (Kapton) with 10^7 W/cm^2 of 351-nm radiation and interpreted his slit deflection data in terms of shock and

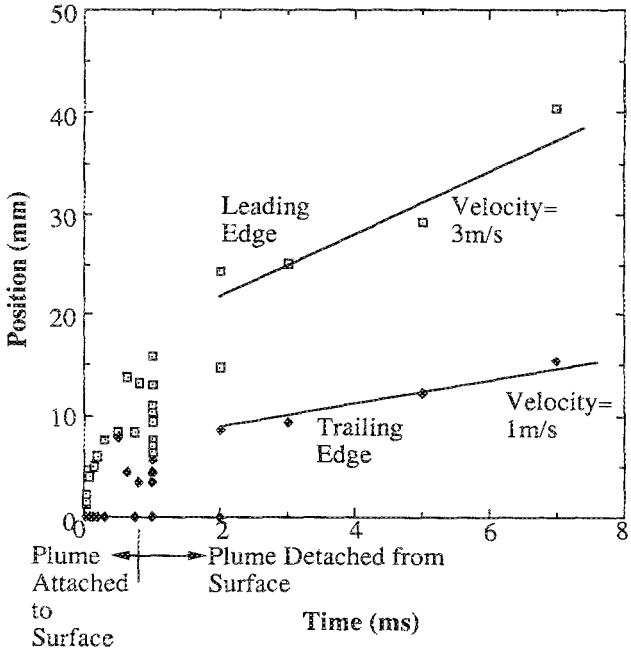

FIG. 3. Plume motion from the ablation of PET in air with 100–150 mJ/cm^2 of 248-nm radiation.

cooling waves. His deflections were at 60 and 80 μs for a probe beam that was 2.5 mm from the target surface, indicating a speed of approximately 30–40 m/s. This is similar to the front velocity of the plume directly observed by us.

Once the plume detaches from the surface its leading edge travels at approximately 3 m/s and its trailing edge travels at approximately 1 m/s. This is consistent with the velocities we measured previously by beam deflection.[1]

Treating the plume as a piston driving a shock and using an average shock velocity c_{shock} we can use the relations to solve for the piston (plume) velocity u_p,

$$c_{\text{shock}} = c\left(\frac{\gamma-1}{2\gamma}+\frac{\gamma+1}{2\gamma}\frac{p_2}{p_1}\right)^{1/2}, \quad (1)$$

$$u_p = \frac{c}{\gamma}\left(\frac{p_2}{p_1}-1\right)\left[\left(\frac{2\gamma}{\gamma+1}\right)\Big/\left(\frac{p_2}{p_1}+\frac{\gamma-1}{\gamma+1}\right)\right]^{1/2}, \quad (2)$$

where c is the speed of sound, p_2 is the pressure behind the shock, p_1 is the pressure in front of the shock, and γ is the ratio of specific heats.

For a fluence of 100–150 mJ/cm^2 with a shock velocity of 370 m/s. Eq. (1) gives $p_2/p_1 = 1.19$. Equation (2) indicates that the piston speed should be approximately 43 m/s in good agreement with the measured average plume velocity of 33 m/s. At higher fluences (above 1 J/cm^2), the piston model ceases to be valid. Fluences of 7–10 J/cm^2 produce an initial observed plume velocity of approximately 200 m/s. The theoretical shock velocity is then 480 m/s compared to an observed shock velocity of approximately 1000 m/s.

As the fluence is increased (for the case of PET), we measure the following x-t scaling for the shocks:

(a) $x \alpha t^{1}$ at 30–300 mJ/cm^2,

(b) $x \alpha t^{0.8}$ at 1 J/cm^2,

(c) $x \alpha t^{0.7}$ at 10 J/cm^2.

This is an expected transition because as the fluence is increased the phenomena should approach the characteristics of the point explosion theory of Zeldovich and Raizer,[11] which for spherically symmetric blast waves indicates that x is proportional to $t^{0.4}$. The energy dependence of the shock velocity was determined by a time-of-flight analysis. We have found, at higher fluences, that the shock velocity follows an $E^{0.2}$ dependence, as is expected from point explosion theory. For the point explosion theory to be valid, the ablated mass must be negligible and the pressure behind the shock must be much greater than the ambient pressure.[12,13] At higher fluences, 10 J/cm^2 for example, the limits of applicability for PET are 6–18 mm. At a lower fluence, 1 J/cm^2, the limits are 4.5–8 mm.

Figure 4 shows a comparison between laser deflection and schlieren photographs for the ablation plume at a fluence of 150 mJ/cm^2. The first part of the deflection trace in Fig. 4(a), beginning at 200 μs, corresponds to the leading edge (LE) and is positive, indicating decreasing density as the plume passes the probe beam. The negative deflection that follows, beginning at 400 μs, indicates an increasing density. At 600 μs the trace returns to 0 coinciding with the trailing edge (TE). Approximating the positive part of the laser deflection trace as a sine wave with a peak of 40 mV and using an average plume velocity of 18 m/s, the laser deflec-

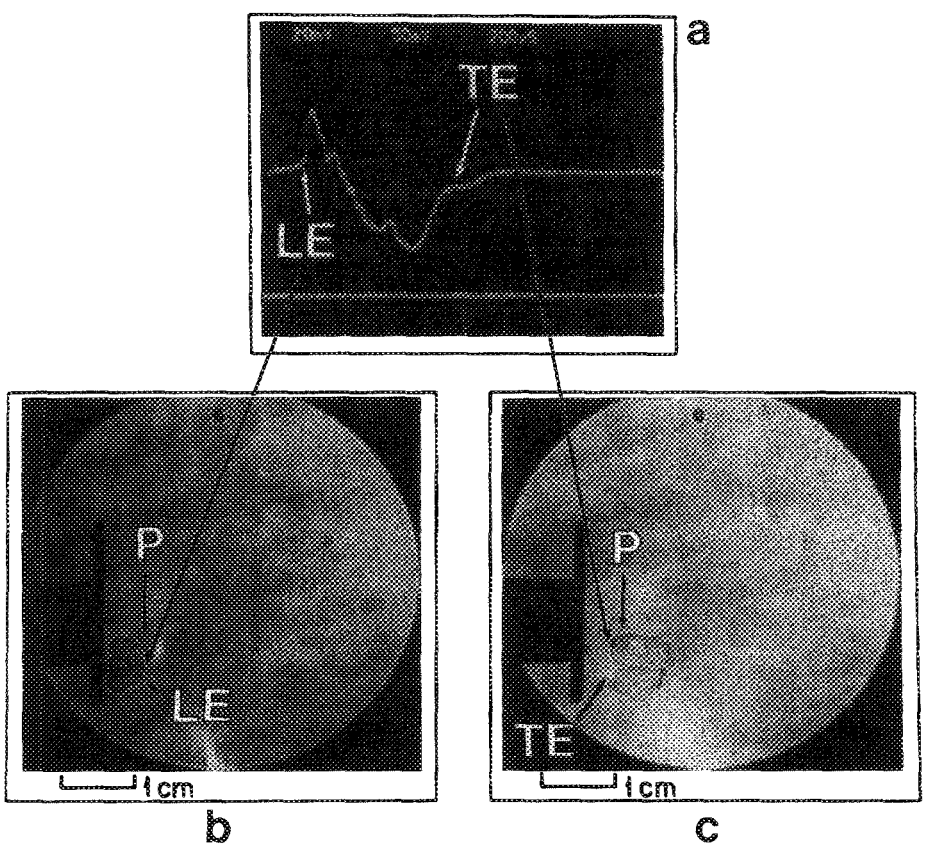

FIG. 4. Comparison between schlieren and laser deflection of PET ablation in air by 150 mJ/cm^2 of 248-nm KrF laser radition. The excimer laser beam was incident from the right of the photo, perpendicular to the target surface. (a) Laser deflection oscilloscope traces: 50 mV/div and 200 μs/div. The probe beam is 5 mm from the target surface. The sensitivity of the detector was 0.087 V/mrad. (b) Schlieren photograph of plume 200 μs after excimer laser pulse. (c) Schlieren photograph of plume 800 μs after excimer laser pulse. The label LE refers to the leading edge of the plume; the label TE refers to the trailing edge of the plume. P refers to the location of the probe beam.

tion measurements show that the plume is a density cavity at 0.5 atmospheric density or 0.6 kg/m^3. This density is an average because the plume is expanding as it passes the probe. Since the plume is expanding very slowly after it detaches from the surface, one could hypothesize that it is close to pressure equilibrium with the surrounding gas. In this case, the temperature of the plume would be 600 K.

IV. CONCLUDING REMARKS

To gain insight into the plume dynamics, experiments were conducted in atmospheric pressure air, N_2, and Ar. It was found, at fluences less than 5 J/cm^2, that the size of the plume in air was always 20%–30% larger than the plume created with the same fluence in N_2 or Ar. This suggests that the heated ambient gas and ablated material mixture is undergoing a chemical reaction and may generate a turbulent diffusion flame.[13] If combustion is occurring, the energetics are comparable to that of the energy deposited by the laser. From the data presented in Ref. 14, at 1 J/cm^2, the energy per ablated mass is 14 kJ/g; a typical heat of combustion is 42 kJ/g.[15] At higher fluences, 6–10 J/cm^2, the plumes generated in each gas are approximately the same size and are very turbulent. At these fluence levels the energy per unit ablated mass supplied by the laser exceeds the maximum that could be supplied by combustion. Furthermore at these fluences we observe, photographically, a very bright flash which supports the possibility of a laser-induced breakdown plasma at the surface.

If one assumes that the laser was the only source of energy for the ablated material, then for the case of Fig. 4, the calculated plume temperature would be 80 K above ambient. If the ablated mass underwent complete combustion, the temperature rise would be 540 K. Assuming pressure equilibrium, we calculated the temperature rise in the plume to be about 300 K above room temperature, which suggests that the ablated material may undergo incomplete combustion. However, further experiments are required to definitively identify the combustion reaction.

ACKNOWLEDGMENT

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