

Laser beam deflection as a probe of laser ablation of materials

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Helium-neon laser beam deflection is used to study excimer laser ablation of polymers and a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor. Density gradients above pulsed laser heated or ablated samples deflect the He-Ne laser beam and this is measured using a position sensitive detector. The technique permits the determination of the laser fluence threshold for ablation both in a vacuum and in air, and the velocity of the ablation products in a vacuum. A model of the thermal deflection at low fluence was developed which enables measurements of thermal diffusivity of the air.

Pulsed ultraviolet (UV) laser photoablation has proven very useful in two types of material processing: material removal such as in the etching of polymers¹⁻⁷ and in material deposition such as in deposition of thin-film high T_c superconductors.⁸⁻¹¹ Diagnostics of the ablation process have been the subject of numerous papers.^{2-7,11} In particular, measurements of the etch rate using a quartz crystal microbalance have been demonstrated.² They allowed the determination of the threshold laser fluence for ablation but would not seem to be universally applicable to nonpolymeric materials such as inorganic solids since the quartz crystal was coated with the polymers.

We demonstrate here that the technique of laser beam deflection is a useful tool for studying the ablation process and provides new information that is complementary to that furnished by other techniques. We show that the ablation threshold can be measured for virtually any material in air (or other fluids) or in a vacuum, and that the ablation product velocity in a vacuum can be determined as well as the air velocity normal to the solid surface in the case of ablation in air. A beam from a low-power cw laser is passed parallel to the substrate surface, but displaced above it by a few hundred microns. A position sensitive detector, located roughly 1/4 m away, measures the deflection angle of the probe beam due to index of refraction gradients in the gas from the pulsed UV laser heating or ablation. In the case of material heating alone, this is commonly called photothermal deflection (PD)¹²⁻¹⁴ or mirage detection¹⁵ and is usually performed with chopped cw radiation. However, recently there have been reports of pulsed PD applications.^{16,17}

Our work extends that done previously by Koren,¹⁸ by Enloe *et al.*,¹⁹ and by Petzoldt *et al.*²⁰ Koren¹⁸ used probe beam deflection above the sample to observe shock waves and cooling waves. However, the slit and photomultiplier detection used did not allow interpretation of the data in terms of both a positive and negative deflection angle, and he did not use the method to identify the ablation threshold. Enloe *et al.*¹⁹ analyzed probe beam deflection as a result of plasma formation from a pulsed laser incident on graphite and polymer surfaces. Material ablation may or may not be accompanied by plasma formation, but the technique can

still be used in the absence of a plasma as shown here. Petzoldt *et al.* used a probe beam deflection method to measure the damage threshold from a pulsed visible dye laser beam on optical materials CaF_2 , MgF_2 , and LiF . Their approach was to measure the acoustic pulse energy as a function of incident beam intensity. The present work also deals with probe beam deflection due to acoustic pulse formation, but emphasizes the distortion of the beam deflection signal from the thermal wave which occurs near the ablation threshold.

The ablation source was a focused beam of pulsed UV radiation from a KrF excimer laser operating at 248 nm wavelength with a maximum energy of 300 mJ/pulse. The excimer beam was apertured by a rectangular slit for best beam uniformity and focused by a cylindrical lens to a rectangular spot. The width of the spot was much greater than the diameter of the probe beam. A probe beam, a HeNe cw laser of 4 mW power focused by a lens ($f = 125$ mm) to a waist of 80 μm , passed parallel to the sample surface oriented normally to the excimer beam and parallel to the long axis of the excimer rectangular spot.

A range of fluences incident on the sample surface was achieved by varying the laser energy per pulse, by attenuating the laser energy with quartz plates ($\approx 10\%$ attenuation per plate) and by changing the distance between the pump focusing lens and the sample surface (hence, varying the pump laser spot size). The error bars in the fluence values are estimated to be less than 10%. In order to make single shot measurements, a calibrated photodiode was used to monitor the energy per pulse of the excimer pump laser. The samples were mounted in a vacuum chamber which was a six-way cross pumped by a turbomolecular pump typically to 1×10^{-5} Torr.

Deflection of the probe beam was measured by a quadrant cell photodiode whose rise time was previously determined to be 50 ns.¹⁹ The samples studied here include graphite, poly(ethylene terephthalate) (PET), polyimide, and bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123).

Figure 1 shows the probe beam deflection signal at low fluence (17 mJ/cm^2) in air at atmospheric pressure for PET, which appears as a rapid rise followed by a slow decay. This signal can be accounted for entirely as a thermal deflection

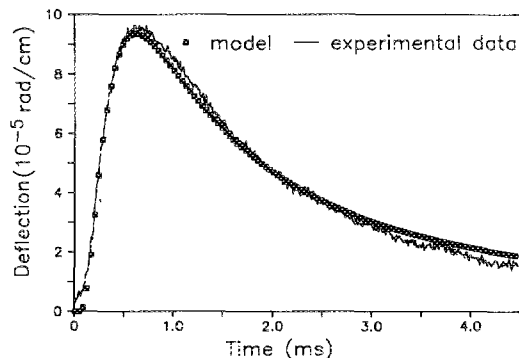


FIG. 1. Single shot laser beam deflection signal (normalized to the path length $L = 1.65$ cm) for PET obtained in air at atmospheric pressure with an excimer laser fluence of 17 mJ/cm^2 . The model data were multiplied by a factor of 0.55 for comparison with the experimental data.

signal. The UV pulse from the excimer laser simply heats the polymer surface and some of this heat subsequently conducts into the adjacent air. The probe beam is deflected due to the time dependent density (and therefore index of refraction) gradient that diffuses through the probe beam path. Figure 1 also shows a deflection signal calculated by a thermal model²¹ where the deflection angle ϕ is given by

$$\phi = -\frac{1}{n} \frac{\partial n}{\partial T} \frac{LE_0 k_g}{4\sqrt{\pi} \rho_g C_g k_s} \times \left(\frac{D_s}{D_g}\right)^{1/2} \frac{|vt-z|}{(D_g t)^{3/2}} (1+\Gamma) \exp\left(-\frac{(vt-z)^2}{4D_g t}\right), \quad (1)$$

where Γ is the thermal mismatch defined as $\Gamma = (e_s - e_g)/(e_s + e_g)$ where e_s and e_g are the effusivities of the solid and gas, respectively, n is the index of refraction, k is the thermal conductivity, D is the diffusivity, L is the overlap length of the probe beam with respect to the excimer beam, E_0 is the absorbed excimer beam fluence, z is the probe-sample separation, and v is the velocity of the gas in the z direction. The agreement between the model which assumes a single ray of the probe beam at height z and the experiment is good using experimental values of the parameters and $v = 0$.

Analysis of the thermal deflection model shows that if the deflection signal is obtained as a function of the probe-sample separation z , it is possible to derive the value of the diffusivity of the fluid above the sample. Specifically, a plot of the time to reach peak deflection versus z^2 should be a straight line whose slope is $1/(6D_g)$. Such behavior was found for PET using a fluence of 12 mJ/cm^2 yielding a value of $D_g = 0.20 \text{ cm}^2/\text{s}$, in agreement within error bars with a previous measurement²² of D_g (0.23) for air at room temperature and atmospheric pressure. Similarly, it can be shown that a plot of the time to reach peak deflection versus pressure at a fixed distance z should be linear, which we observe over a pressure range of 2 to 760 Torr; this yielded the same value for D_g . We believe that these methods of measuring the thermal diffusivity have not been reported before, although Loulergue and Tam have previously reported²³ measurements of the diffusivity of a doped, unconfined hot gas using a collinear beam deflection technique.

Figure 2(a) shows the deflection of the probe beam in

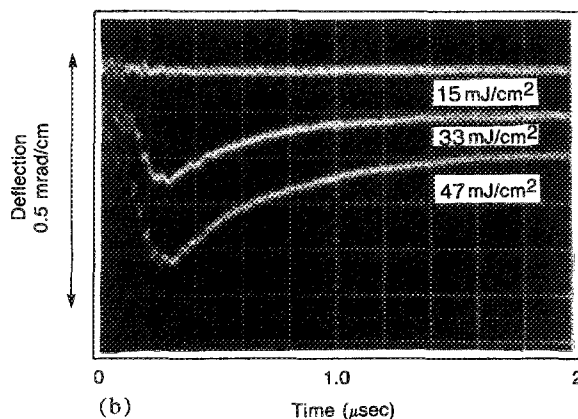
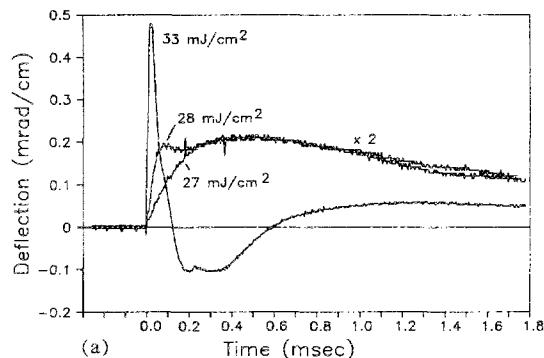


FIG. 2. Single shot normalized laser beam deflection signal of PET (a) in air at atmospheric pressure obtained with an excimer laser fluence of 27, 28, and 33 mJ/cm^2 . (b) same as (a) but obtained in a vacuum at 15, 33, and 47 mJ/cm^2 .

air for three different values of the excimer laser fluence, 27, 28, and 33 mJ/cm^2 . Below the ablation threshold, the deflection signal has no zero crossing (see the curves for 27 and 28 mJ/cm^2). Although not shown in the figure, we have verified that the deflection amplitude scales linearly with excimer fluence from 11 to 22 mJ/cm^2 , indicating a constant fraction of energy deposition into the solid which conducts into the air. Above the threshold, the probe beam deflection has a zero crossing (see the 33 mJ/cm^2 curve) and a large amplitude, rapid component. We believe that the distorted shape of the deflection signal is due largely to the convective plume of the gaseous air/ablation product mixture. It is possible, however, that some of the deflection signal is due to particulates formed during or slightly after material ablation commences. The particulates would be expected to carry heat and could therefore deflect the probe beam. Further work to clarify this point is in progress and will be reported in a separate paper.

The deflection signal at earlier times (less than $1 \mu\text{s}$) showed an acoustic wave, similar to that observed previously.¹⁶ The acoustic wave also became distorted,²⁰ however, as the fluence was raised through the ablation threshold.

Figure 2(b) shows the deflection signal obtained in a vacuum for three fluences, 15, 33, and 47 mJ/cm^2 . The deflection is much more rapid and in the opposite direction to the low-fluence deflection in air. The amplitude of the deflection increases nonlinearly as the fluence is increased through the ablation threshold. A time-of-flight analysis was applied

TABLE I. Ablation threshold fluence (mJ/cm^2) using 248 nm.

Material	Present work		Previous work		Reference
	in vacuum	in air	in vacuum	in air	
PET	20-24	28-33		22 22 30	2 6 3
Polyimide	20-30	27-35		27 31 55 65	7 3 4 6
Graphite	11-25	35-45			
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	100-120	100-120	110 350-400		9 11

to the vacuum deflection data to obtain ablation product velocities for the four samples studied here on the order of 1-3 km/s, in agreement with previous measurements^{5,11} by other techniques at 248 nm, but somewhat lower than the velocities measured previously²⁴ at 193 nm.

The ablation threshold in a vacuum was taken to be the fluence at which the deflection signal increased nonlinearly and is shown in Table I. The ablation threshold in air is taken to be the fluence at which the deflection signal changes drastically [Fig. 2(a)]. These values shown in Table I agree well with the threshold fluences measured previously by others using conventional methods, lending credence to the present method of measuring the threshold fluence. The threshold for ablation in a vacuum is in general slightly lower than that in air.

The deflection signal shown in Fig. 2(a) at $33 \text{ mJ}/\text{cm}^2$ is reminiscent of deflection signals shown in Ref. 13 where crossed beam photothermal deflection was used to measure gas flow velocity above a laminar jet. In that work it was shown that the time delay for the deflection signal to cross zero could be used in a time-of-flight analysis to measure flow velocity with good accuracy. Assuming that the distorted deflection signal is due to convection of the gaseous ablation product/air mixture, we applied a time-of-flight analysis to the data. The velocity measured by this method is then the velocity of the air/ablation products mixture normal to the surface. This was done for PET ablation in air, He, and Xe as a function of excimer beam fluence at a height of 300 μm . The measurements were made at fluences from 38 to 51 mJ/cm^2 , where it was found that the fluid velocity increased linearly with fluence and ranged from 2.2 to 4.9 m/s for air, from 1.4 to 2.3 m/s for Xe, and from 29 to 35 m/s for He. Additional measurements at larger distances from the sur-

face are in progress and will be reported separately in the future.

In summary, laser beam deflection was applied to pulsed UV laser ablation of polymers and a ceramic superconductor allowing the determination of the threshold ablation fluence, both in air and in a vacuum. A thermal model valid for low fluence enabled measurements of the diffusivity of air, in agreement with prior work. The method also yielded the ablation product velocities in a vacuum which were on the order of a few km/s, in agreement with previous measurements by others. For ablation in air and Xe, convection velocities of the fluid normal to the surface were a few m/s, and roughly 30 m/s for He. The technique seems to be applicable to virtually any material.

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