AIP | Applied Physics Letters

Comment on ''Nanosecond photoacoustic studies on ultraviolet laser ablation of organic polymers''

L. M. Kukreja and P. Hess

Citation: Applied Physics Letters **62**, 205 (1993); doi: 10.1063/1.109316
View online: http://dx.doi.org/10.1063/1.109316
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/62/2?ver=pdfcov
Published by the AIP Publishing

Comment on "Nanosecond photoacoustic studies on ultraviolet laser ablation of organic polymers"

L. M. Kukreja[a] and P. Hess
Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, W-6900 Heidelberg 1, Germany

(Received 16 March 1992)

It is important to understand the time evolution of UV laser-induced polymer ablation with respect to the onset and duration of the exciting laser pulse. An elegant method for measuring the onset time of ablation has been introduced by Dyer and Srinivasan[1] (DS), who detected the transient stress waves produced by UV laser irradiation with a broad bandwidth polyvinylidenefluoride (PVDF) piezoelectric foil transducer. On the basis of their ablation experiments, DS concluded that the ablation begins within about 4–6 ns of the start of the laser pulse. The results have been interpreted as evidence for ablative photodecomposition of the polymers because the temperature rise in the observed short time before the onset of ablation is probably insufficient to decompose the material thermally.

Recently we have measured the onset time of particle emission for polyimide and PET samples induced with XeCl (308 nm) and KrF (248 nm) laser radiation using a novel time resolved optical detection technique.[2] In this technique a HeNe laser beam of 200 μm effective diameter touching the polymer surface was employed to register the onset of ablation by detecting its attenuation due to scattering and absorption by the ablation products leaving the surface. The attenuation signal was detected by a fast pin photodiode (response time 2 ns) using a digital oscilloscope with 500 MHz sampling rate. Using this method we found that the onset times were much longer than those reported by DS and that they varied very strongly with laser fluence, with ablation commencing during the laser pulse only at high fluences.

The experimental setup used for the photoacoustic detection of the ablation process was close to that described by DS. A 9 μm thick PVDF foil (Solvay), coated with 0.4 μm thick aluminum electrodes on both sides, was employed as a piezoelectric transducer. It was bonded to a 6 mm thick impedance matching stub of Lucite. The present experiments were performed on 7.5 μm thick polyimide (Kapton) sheets whose contact with the front surface of the PVDF foil was maintained by either pressure or grease. A XeCl excimer laser was used for excitation. The acoustic signals were recorded by means of a digital storage oscilloscope with an overall response time of about 4 ns.

Figure 1(a) shows the acoustic signal in the case of a pressure-contact PVDF foil transducer at a fluence of about 150 mJ/cm^2, which is delayed by about 200 ns from the start of the laser pulse. Figure 1(b) shows the corresponding attenuation signal detected by the optical probe beam method. The onset time of the delayed signal was found to decrease nearly exponentially with laser fluence and to depend on the optical absorption coefficient of the polymer for both methods.

Besides the case where the polymer sheet was almost perforated after several ablation events and fast signals originated from a direct irradiation of the PVDF foil transducer, fast signals were also observed in the case of a grease-contact PVDF foil. When the pump laser fluence was increased to about 1 J/cm^2, this fast signal changed its shape from monopolar to bipolar or even tripolar.

The results are consistent with the following interpretation of the observed fast and delayed acoustic signals. The fast signal which develops essentially with the time constant of the detection system, is considered to be due to

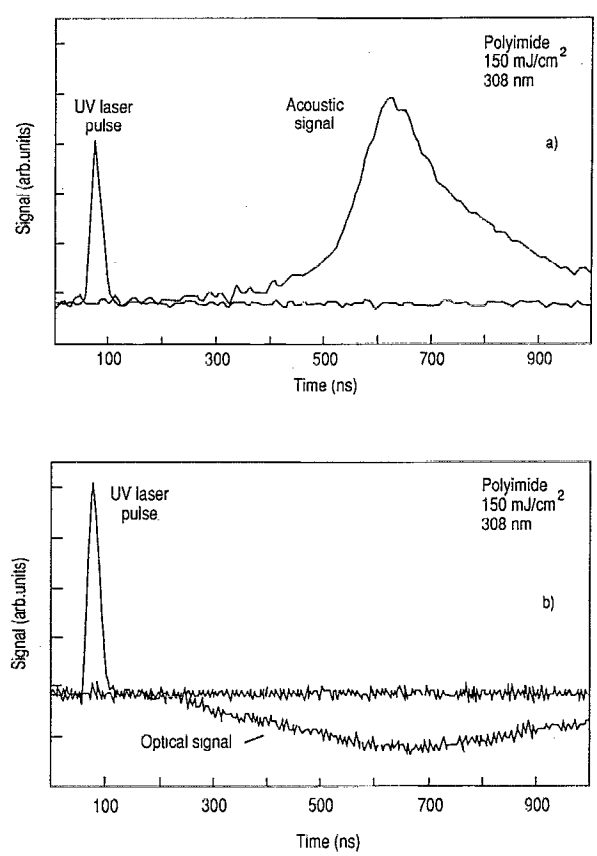

FIG. 1. Comparison of onset times of ablation measured by (a) PVDF foil transducer and (b) probe beam attenuation.

[a]Permanent address: Laser and Plasma Technology Division, Bhabha Atomic Research Center, Bombay-400 085, India.

 0003-6951/93/020205-02$06.00

a thermoelastic excitation mechanism. This signal is detected only in the case of effective coupling between the polymer and the foil transducer, e.g., by grease, and lasts only for a relatively short time. The fluence dependent onset time of the delayed unipolar signal shows the characteristic behavior of a thermally activated decomposition process and is interpreted as due to the recoil momentum of the ablation products. It is stronger than the fast signal and can also be observed in the case of pressure contact. The delay times agree within experimental error with those measured by the optical attenuation method. Ablation commences within the duration of the laser pulse only at high fluences; for these cases the fast and delayed signals overlap. According to this interpretation of the acoustic signals, fast ($\sim$ns) onset times of ablation are observed only for large fluences ($\sim$1 J/cm^2). At lower fluences these onset times are much longer than previously reported.

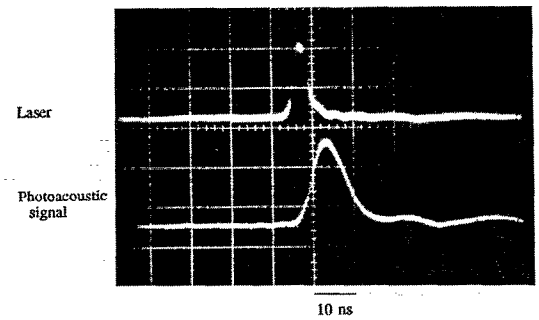

FIG. 1. Oscilloscope trace of laser pulse and photoacoustic signal from Kapton H film (25 μm thick) irradiated with XeCl pulse.

[1]P. E. Dyer and R. Srinivasan, Appl. Phys. Lett. **48**, 445 (1986).
[2]L. M. Kukreja and P. Hess, in *Photoacoustic and Photothermal Phenomena III*, edited by D. Bicanic (Springer, Berlin, Heidelberg, 1992), p. 200.

Response: Kukreja and Hess (KH)[1] describe the use of nanosecond photoacoustic techniques to study excimer laser ablation of polymers and claim to obtain significantly different results from our original letter.[2] They observe long delays and broad ($\sim$200 ns) pulse widths and suggest that the short ablation times we reported are due to complete etching of the polymer such that the laser directly irradiates the piezoelectric film transducer. We were well aware of this as a potential problem and indeed some brief experiments were conducted to investigate it. We can categorically state, however, that in none of our reported experiments were films subjected to more than a few shots and in *no case* did anything approaching complete film removal occur.

Other relevant checks were also made. One was to rule out the possibility that a near-infrared (IR) lasing component in the excimer laser emission[3] penetrated the film and directly excited a phantom ablation signal (most polymers are transparent in the near-IR). This possibility was eliminated by observing that signals were absent when an IR transmitting, ultraviolet (UV) laser absorbing plastic sheet was placed in the beam. Furthermore, simultaneous UV laser ablation of two polymer films bonded to form a step edge gave two ablation peaks with a time delay consistent with the acoustic transit time. The signals were thus deduced to originate at the front film surface and could not have arisen from direct IR irradiation of the piezoelectric film. It is also relevant that the band width of the acoustic detection system was found in separate experiments to be at least 150 MHz.[4]

Strong evidence for the prompt nature of ablation comes from our work on the more weakly absorbing polymers [e.g., polymethymethacrylate (PMMA) in Ref. 2]. These exhibit a clear thermoelastic response below threshold which merges into the ablation signal *during the pulse* when the threshold is exceeded (Fig. 3, Ref. 2). It was only for this system (PMMA at 193 nm) that a tentative conclusion was drawn regarding a substantial photochemical contribution to ablation.

Our photoacoustic studies provided the first clear evidence that ablation commences during the laser pulse. Since then other techniques have been used which confirm this finding, e.g., transient laser reflection, transmission, and fast imaging.[5] Kukreja and Hess do not attempt to explain how their results can be reconciled with this substantial body of evidence.

Following receipt of Kukreja and Hess's comment we repeated one experiment with the transducer geometry described in Ref. 2 using a 6 ns (full width at half maximum), 157 mJ cm^{-2} XeCl laser to irradiate a polyimide film. (Kapton H, 25 μm thick as no 7.5 mm film was available.) The laser and acoustic signals were synchronized as previously described[2] and displayed on a Tektronix 7844 oscilloscope. The results (Fig. 1) clearly confirm that ablation commences during the pulse in keeping with our earlier findings. Ablation was on a fresh surface and four sequential pulses were overlaid on the same site. It is evident that the pulse is short ($\sim$10 ns) and also has a short delay which does not change with number of pulses, in sharp contrast to the claim made by Kukreja and Hess. Pulse reflection sequences between the rear of the stub and front of the film showed they propagated at the longitudinal bulk wave velocity for Lucite and were thus acoustic in nature.

Kukreja and Hess draw support for their findings from the apparent similarity between their acoustic and probe beam detection signals. No details of the latter system are