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Study of UV Laser Ablation by Optothermal Methods

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Abstract. Optothermal methods for the study of UV laser ablation are discussed. Pyroelectric and photoacoustic measurements for PMMA and Al irradiated at 193 nm are reported. Ablation thresholds are estimated. The different mechanisms contributing to the signal generation are discussed.

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The interaction of intense laser pulses with solid materials is of considerable current interest in view of the development of new technologies. Interesting possibilities are offered by excimer lasers generating light in the UV spectral range. The process of direct photodecomposition is at the centre of current investigations. Intense laser radiation may etch a wide range of materials including metals, semiconductors, polymers and biological tissues. The spontaneous removal of polymeric material has been termed "ablative photodecomposition". The depth and the size of the hole may be well controlled by the operating conditions and the optics of the laser. The ablation may play an important role in microelectronics, microfabrication and surgery [1, 7] and, in future, in microbiology. However, the process of UV ablation is not yet fully understood and, moreover, there is no simple method for monitoring ablation in practical applications.

Many of the material parameters influencing the thermal balance of the system are changed during ablation. Thus optothermal methods can effectively help in the study of these processes. Using very thin thermocouple the authors [3] have established not only the threshold of ablation but simultaneously demonstrated non-thermal feature of the photodecomposition. A significant fraction of light energy above the threshold is utilized in the disruption of chemical bonds and also contributes to the thermal and the kinetic energy of ablated material as shown in [4] using a pyroelectric detector. A rapid increase of the acoustic emission above the threshold was also observed. By investigating the shape of the acoustic pulse above the threshold, it was determined [2] that ablation occurs within the time span as the laser pulse.

Optothermal methods measure the heat produced by the absorption of light energy in the sample. They include various different techniques such as direct measurement of the temperature by a thermocouple, photoacoustic gas cell or photothermal beam deflection techniques, etc. The mechanism of signal generation and all the factors that can influence the signal in the different methods must be taken into account to avoid possible misinterpretation.

The thermocouple signal corresponds to the temperature change at the point of contact to the sample. If its dimensions are much less than the characteristic dimensions of the irradiated spot and the sample thickness is comparable or less than the thermal diffusion length, the thermocouple is considered to be a point detector. In this case the signal is proportional to the fluence. It is necessary to have a good thermal contact with the sample and to prevent direct irradiation of the thermocouple by the excitation light.

The pyroelectric detector acts as an integral detector with an output signal that is sensitive to the change of energy. Samples must also be thermally thin to assure effective passage of heat to the detector. Samples can be sprayed or bonded directly onto its surface electrode.

The mechanical stress generated in the sample material after light absorption is detected by a piezoelectric transducer. The resulting signal due to the ablation can be generated not only thermoelastically

but also as a result of reactive forces of the ejected material fragments.

Photothermal beam deflection works as a line detector with an output signal corresponding to changes of the refractive index along the interaction path of the monitoring beam. These changes may be caused not only by the temperature rise but also by the presence of outgoing particles and gases in the interaction region.

The situation is very complicated in a gas photoacoustic cell. Normally the signal depends on the energy of the light beam. In the case of ablation, the signal may originate from a direct acoustic component in addition to the pressure component caused by the gas heating from the surface of the sample. Pressure changes can result from the gas production. The heating conditions may also be changed as hot fragments are ejected. Attention must be paid to possible contamination of the input window by ablated fragments. They can absorb subsequent pulses and continue to photodecompose. The signal is expected to be dramatically changed in the region of ablation threshold, since here it can be influenced by many factors. One of the advantages of the gas photoacoustic cell is the possibility to investigate samples in different forms.

In our paper we will deal with a study of the UV ablation of polymethylmethacrylate (PMMA) and aluminium using a pyroelectric detector and a gas photoacoustic cell.

1. Experimental

The experimental arrangement is shown schematically in Fig. 1. The source of UV radiation is a LUMONICS TE-860–ArF excimer laser (193 nm), pulse duration 8–10 ns (FWHM), beam divergence 1.2×6 mrad (FWHM) and pulse to pulse reproducibility 8%. A spatially uniform part of the laser output beam is selected by an iris diaphragm. A small portion of the beam energy is deflected to the calibrated pyroelectric detector which monitors the energy in the pulse. The beam can be attenuated using two quartz wedges and it is focused by a CaF_2 lens ($f = 200$ mm) onto the pyroelectric detector covered with the sample or alternatively on the sample in the photoacoustic gas cell of our own construction. The fluence on the sample surface is controlled by varying the distance between the lens and the sample. The fluence is determined from the beam energy and the irradiated area. The pyroelectric detectors (PZT ceramic) are homemade. The detectors monitoring light energy are covered with a black paint and are energy calibrated. An Ag electrode of the measuring detector was spin coated by thin layer of PMMA dissolved in dichloroethane or thin Al foil (30 μm) was glued by cyanoacrylate. The samples for the gas photoacoustic measurements were prepared in the same way on the quartz sample holder. The output pyroelectric or photoacoustic signals and the signal from the energy monitor are measured by a Tektronix two channel memory oscilloscope. The pyroelectric output pulse is characterised by a relatively slow leading edge (typically several ms) caused by the heat conduction through the sample, after which it falls very slowly due to sample cooling. There is no change in the pulse shape upon changing the fluence. That is why the peak value of the pyroelectric signal is taken to represent the evolved heat. The signal of the photoacoustic gas cell has the shape of damped oscillations, as was observed similarly in [6]. The maximum of the first peak was taken.

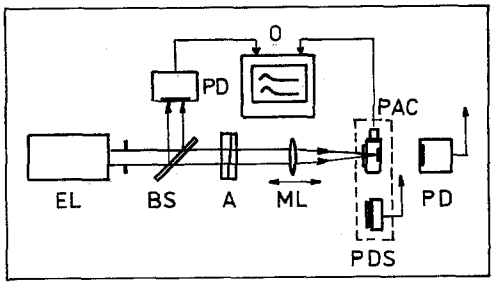


Fig. 1. Experimental setup: excimer laser (EL), beam splitter (BS), attenuator (A), movable lens (ML), pyroelectic detector – energy monitor (PD), pyroelectric detector with the sample (PDS), photoacoustic cell (PAC), oscilloscope (O)

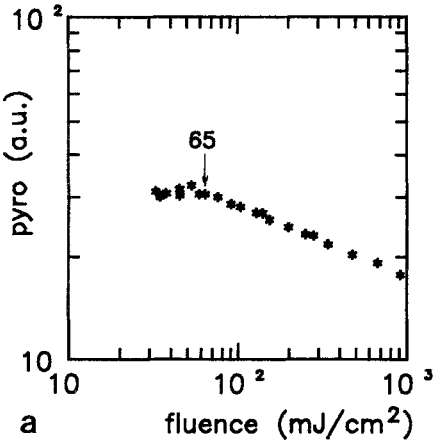
2. Results and Discussion

The dependences of the pyroelectric and the photoacoustic signal of PMMA on fluence are plotted in Fig. 2a and 2b, respectively. The signals were corrected for the energy changes in the pulses. The pyroelectric signal remains constant up to 65 mJ/cm^2. Increasing the fluence the pyroelectric signal falls. The position of the break point on the curve is in very good agreement with the ablation threshold deduced from etch rate measurements [5, 8]. According to [9] the photon flux threshold defines the concentration of photons absorbed per unit time required to overcome the various relaxation paths. Above the threshold, only part of the absorbed energy is converted into heat. The remaining part is used for direct bond scission so that the thermal loading is constant in the ideal case. According to this model the thermal energy evolved below threshold is

$$Q \sim F \cdot S \cdot (1-R),$$

where F is the fluence, R the reflectivity and S the irradiated area. Above threshold this becomes

$$Q_T \sim F_T \cdot S \cdot (1-R) = (1-R) \cdot E \cdot F_T/F,$$



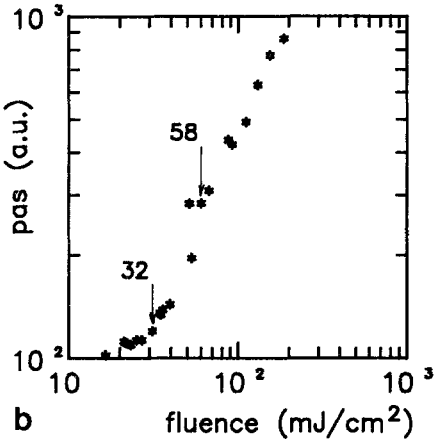
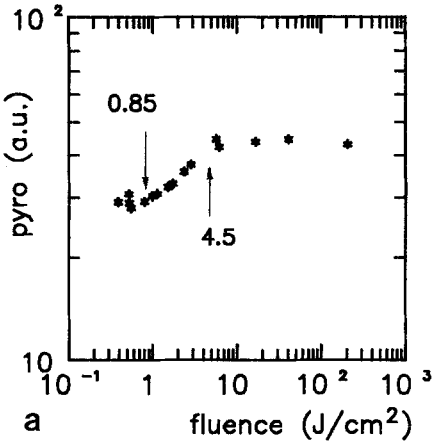


Fig. 2a, b. The peak pyroelectric a and photoacoustic b signal vs. laser fluence for a PMMA-coated pyroelectric detector and sample holder, resp.



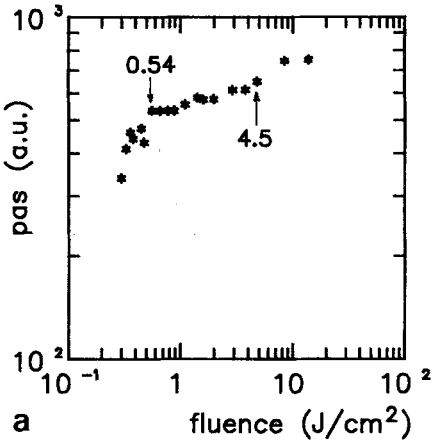


Fig. 3a, b. The peak pyroelectric a and photoacoustic b signal vs. laser fluence for Al foil glued onto the pyroelectric and sample holder, resp.

where E is the beam energy and the subscript T means threshold values.

According to this model, the pyroelectric signal should decrease as $1/F$ above the threshold for constant input energy. The slope of the experimental curve above the threshold (Fig. 2a) is not -1 but smaller (~ -0.45). This means that the thermal loading is not constant, but continues to rise.

The gas cell photoacoustic signal increases moderately in the region of low fluences. It changes rapidly between 32 and 58 mJ/cm^2. The position of the begining of the curve breaking is in good agreement with previous observations that ablation is occurring in this subthreshold region [2]. In this region the LIF signal of evolved C_2 was also observed [8]. Above 58 mJ/cm^2 the PA signal rises almost linearly with the fluence. Due to the decrease of thermal relaxation above threshold – as confirmed by pyroelectric measurements – the gas cell PA signal should decrease as well. As we proposed in the introduction, other non-thermal mechanisms can also contribute to the PA signal. With respect to the behaviour of the signal above threshold, it is evident that these mechanisms become dominant. The main mechanism of the pressure rise may be the evolution of gaseous products during the ablation.

The mechanism of the interaction of UV radiation with the metal is probably different to the case of organic polymers [10]. This is confirmed by the behaviour of the pyroelectric and the photoacoustic signal of Al foil (Fig. 3) which differs from that of PMMA. The pyroelectric signal remains constant up to a fluence of 0.85 J/cm^2. Above this value it increases until the fluence reaches 4.5 J/cm^2 and then remains almost constant. The amount of the signal increase corresponds to 1.5 times the rise in thermal energy released in the sample. For fluences above the first curve breaking a plasma spark was observed. (Typical fluences for plasma creation by UV radiation are 0.5–5 J/cm^2 for metals). The signal increase may be

explained by the formation of an electron plasma because of the increase of the absorption coefficient and the good thermal conductivity of the plasma.

The PA signal of the Al foil is complicated. It also displays two step-like increases minimally. The fast increase in the low fluence region could be explained by liberation of molecules adsorbed on the sample surface. The first curve break point is at a value of 0.54 J/cm^2. The subsequent signal rise should correspond to the change of the absorption coefficient. The signal increase above threshold is not as high as in the case of the PMMA sample.

3. Conclusion

In conclusion, we have presented measurements demonstrating the usefulness of optothermal methods for studying UV laser ablation processes. It was confirmed that a part of energy above threshold is used (in the case of PMMA) to produce bond breaking. It was observed simultaneously that heating of the sample is further increased above the threshold. The mechanism of ablation of Al is rather different, and thermal production is raised above the threshold. It has been demonstrated with these examples that optothermal methods are available for the study of ablation. However the interpretation of the results must include all possible mechanisms of signal generation.

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