TIME-RESOLVED SPECTROSCOPY AND
NANOSECOND PHOTOGRAPHY OF LASER
ABLATION PROCESSES OF POLYMERS

HIROSHI FUKUMURA and HIROSHI MASUHARA
Department of Applied Physics, Faculty of Engineering, Osaka University,
Suita, Osaka 565, JAPAN

Laser ablation is recognized as one of promising methods for
microfabrication of polymers. Irradiation by an intense excimer laser
produces a high density of excited states and reaction intermediates,
causes a temperature rise, removes surface layer, and gives rise to
morphological changes. This nonlinear photochemical behaviour was
investigated by nanosecond time-resolved spectroscopy and nanosec-
dond dynamic photography just upon laser ablation.

1. Introduction

Irradiation with an intense laser pulse on a polymer surface easily pro-
duces etching of the surface to a depth of a few microns. This phenomenon
was named "laser ablation" by Srinivasan et al.[1], and the application has been
studied extensively as a noncontact surface processing method. Many prob-
lems, however, remain unsolved to make the ablation process fit for practical
use. Not only the etched depth but also the roughness and adhered residues
after ablation are considered to depend on polymer matrix, ambient gas, the
wavelength of laser, the intensity, the pulse width, and so on. This implies that
the mechanism can not be explained simply with instantaneous photo-decomposi-
tion only yielding products ranging from atoms to small molecules. In order to
clarify the mechanism of the ablative surface processing, we believe that a
study on dynamics of electronic excited states is indispensable.

Our approach to study the mechanism is the use of dopant which can absorb laser light and induce the morphological change [2]. Various kinds of combinations for dopant and polymer matrix are possible, so that photochemical as well as photophysical processes can be controlled. When aromatic molecules are chosen as dopants, it is also possible to monitor the dynamics of electronic excited states and reaction intermediates with time-resolved spectroscopy. Consequently, molecular and electronic aspects of laser ablation phenomena can be elucidated in detail. In this contribution we describe our recent studies on laser ablation of doped polymer systems studied by using nanosecond time-resolved spectroscopy and nanosecond dynamic photography.

2. Time-resolved emission spectroscopy

The dynamics for excited singlet states \( S_n \) as well as for emissive products of ablation can be monitored with time-resolved emission spectroscopy. Details of the measurement system are described elsewhere [2,3]. By using a streak camera system (Hamamatsu C2830/C3140), both emission spectra at a time region and temporal behaviour of a wavelength are obtained from a three dimensional image. Hence, one-shot irradiation of laser pulse to a polymer surface is sufficient to get the results, and the system is suited to observe the present irreversible phenomena.

When porphyrin derivatives were chosen as dopants, an irreversible swelling or etching of the irradiated surface took place depending on the laser fluence [4]. The rough surface and many holes of micro-meter order were observed on the ablated surface. This implies that gas bubbles are generated beneath the surface in addition to the surface melting. Figure 1 shows time-resolved emission spectra just upon laser ablation of a tetraphenylporphyrin-doped PMMA film. Irrespective of the laser fluence, the dopant fluorescence (650-750 nm) was observed in the time range of laser pulse irradiation (FWHM 15 ns). At a fluence of 2.8 J/cm², an emission due to fragmented radical (C2: 474, 517, 564 nm) was detected. This radical emission appeared after fluorescence decay. It is therefore obvious that the small molecular fragments were generated at a few tens nanoseconds after irradiation. In the case of lower concentration of the dopant, the radical emission was not detectable while the irradiated surface was etched to several micrometers. Thus, the radical production is not essential in porphyrin-sensitized ablation but thermal effect may be
predominant in the ejection of decomposed polymer.

This kind of time delay for the generation of atoms and fragments was observed also in laser ablation of poly(N-vinylcarbazole) [5] and silicon-containing polymers [6]. A possible explanation for the delay is that molecular fragments ejected from polymer surface are decomposed in air yielding the emissive species. Although detectable species are limited, this spectroscopy provides us the time scale of ablative decomposition to study the mechanism of laser ablation.

![Time-resolved emission spectra](image)

**Fig. 1** Time-resolved emission spectra just upon laser irradiation (351 nm, 15ns) for tetraphenylporphyrin/PMMA film: (a) 2.1 J/cm², (b) 2.8 J/cm². The gate time is given in the figure when the time zero is defined as the maximum intensity of the laser pulse at the detector.

3. Time-resolved absorption spectroscopy

The sensitivity of absorption spectroscopy is generally lower than that of emission spectroscopy, and also the experimental setup is more complicated because excitation pulse and monitor light should be arranged well. This tech-
nique is, however, indispensable to detect non-emissive intermediates like triplet states ($T_n$), radicals and so on. A schematic diagram of the setup is shown in Figure 2. The monitor light source was a 150 W DC Xe arc lamp which was additionally pulsed (FWHM 200 μs) to synchronize with laser pulse. The light was passed into the laser-irradiated region on a sample film and detected by a streak camera system equipped with a polychromator. The detection system was the same with one used for the emission spectroscopy described above.

![Schematic diagram of the streak camera system](image)

Fig. 2 A schematic diagram of the streak camera system to measure transient absorption upon laser ablation.

While a PMMA neat film can be ablated with 248 nm laser irradiation, doping of aromatic molecules generally reduced the ablation threshold from 500 - 600 mJ/cm² to 200 - 300 mJ/cm². Hence, it is obvious that the light absorption by the dopant molecules causes the ablation of polymer matrix as far as the fluence is below the threshold of neat film.

Figure 3 shows the result obtained for biphenyl-doped PMMA film just
upon laser ablation [7]. The transient absorption spectra observed during laser excitation has a peak at 360 nm. The transient species can be assigned to the T1 state of biphenyl. It should be noted that no other species of reaction intermediates were detectable in this time region. After the rapid decay of the T1 state, another broad absorption appeared instead only when the laser fluence was above the threshold. The absorption spectrum had no peak, and the shorter the wavelength was, the larger the intensity of the absorption was. The delayed component can be interpreted as a scattering of the monitor light by decomposed particles. The size of the particles should be larger than the wavelength of the monitor light. The ejection of the particles may be in parallel with progress of ablation, so that morphological change may occur in the time region of a few tens nanoseconds after laser irradiation. Such information is quite important to clarify the dynamics of laser ablation.

Fig. 3 Time-resolved absorption spectra just upon laser irradiation (248 nm, 15 ns, 360 mJ/cm²) for biphenyl/PMMA film: (a) -11 ~ 26 ns, (b) 100 ~ 137 ns.
4. Nanosecond dynamic photography

Time-resolved observation of the morphological change of a polymer surface just upon the ablation can provide us space-resolved information to understand the mechanism. Several attempts have been performed to visualize the phenomena for PMMA [8,9], polyimide [10,11], poly(ethylene terephthalate) [11]. We also applied a similar technique to observe laser ablation of PMMA films doped with biphenyl [12]. Figure 4 shows a schematic diagram of the measurement system. A KrF excimer laser (248 nm, 18 ns) was employed to ablate the surface, while fluorescence from rhodamine solution excited by a XeCl excimer laser (308 nm, 30 ns) or by the second harmonics (532 nm, 10 ns) of a Nd³⁺:YAG laser was used as a probe light for photographic observation. A time delay between the ablation and the probe pulses was adjusted with a delay and pulse generator. The time delay was monitored with an oscilloscope equipped with two photodetectors. The time-resolution of the photographic observation depends on the pulse duration of the probe pulse (ca. 30 ns).

Fig. 4 A schematic diagram of the measurement system for nanosecond dynamic photography.
Laser ablation of biphenyl/PMMA film is described here briefly as an example. As shown in Fig. 5, no change at the irradiated surface was observed when the delay time was 0 ns. Fragment ejection started at 50 ns after excitation, evolved into an opaque stream along the normal direction, and continued until 10 μs. The dimensions of ejected materials should be larger than the wavelength of probe light. This implies that the polymer matrix was not decomposed completely to atoms and small molecules. The velocity of the ejected materials was estimated to be 160 m/s at the laser fluence of 1.3 J/cm². This velocity is almost the same as reported for a PMMA neat film with a 248 nm-laser pulse of 2.8 J/cm² [9]. It is obvious that the electronic excitation energy of biphenyl molecules was converted to the kinetic energy of the ejected material.

The result also indicates that the ejection of the decomposed products does not occur instantaneously during laser excitation. This is consistent with the transient absorption spectral data, namely, the continuum absorption spectrum covering the whole visible wavelength region emerged in a hundred ns as described above.

![Image](248.png)

**Fig. 5** Photographs for the surface of biphenyl/PMMA film at different time delays after the laser irradiation (248 nm, 15 ns, 600 mJ/cm²).
5. Conclusion

On the basis of the present results, it is confirmed that the generation of Si and Ti was predominant at the first half of a laser pulse even upon the laser ablation. These excited states, however, decayed quite rapidly within the laser pulse, and the material ejection was observed after the time lag of a few tens of ns. While the mechanism is complicated and remains unclear from molecular viewpoint, we believe that the present approach with time-resolved measurement is very fruitful.

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References