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Nanosecond time-resolved interferometric study on morphological dynamics of doped poly(methyl methacrylate) film upon laser ablation

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A highly sensitive nanosecond time-resolved interferometry was developed and applied to study dynamics of morphological changes of a thin poly(methyl methacrylate) film doped with biphenyl upon laser ablation. It was confirmed that morphological changes started during a nanosecond excitation laser pulse and then followed by an ejection of ablated polymer fragments. Even below the ablation threshold, a transient expansion of the polymer film, followed by slow contraction, was observed. New features of laser ablation dynamics were clarified. © 1994 American Institute of Physics.

Laser ablation of organic materials with intense ultraviolet excimer laser excitation is of great interest not only for application, but also as a unique physicochemical phenomenon. It has been demonstrated that ablation has a high potential for fabrication of microstructures, modification of material surface, deposition of thin film material, and so on. It is indeed a nonlinear process with respect to the laser fluence, and etching of material surfaces was induced when the fluence exceeds a threshold. For the last decade, a variety of experiments were carried out and many ablation models were proposed, which still has not succeeded in describing characteristics of laser ablation. As interactions between polymer and laser light lead to rapid and large morphological changes in entire polymer matrices, for modeling of laser ablation, it is essential to know dynamics of morphological changes. Some methodologies with a time resolution of picosecond to millisecond and a spatial or vertical resolution of submillimeter to micrometer were developed for their direct observation: ultrafast imaging, schlieren photography, and holographic interferometry. Most of them were concerned with the ejection behavior of ablated plumes and fragments, while no study has been given for morphological changes of polymer surface during or immediately after the excitation pulse. Particularly, at a fluence below the threshold, much information was not available as far as we know. All these results were due to the lack of time-resolved methodology which has sufficient vertical and spatial resolution.

As Michelson interferometry is a high-sensitive method to the surface profiling, we considered that an improvement of its time resolution would be extremely useful for the study of morphological dynamics upon laser ablation. In the present work, we have developed a new method of nanosecond time-resolved interferometry (TRI) by using pulsed laser as a probe light source. As it is a time-resolved interferometric topography, it can clarify a morphological change of several tens of nanometer with a high temporal resolution of several nanoseconds.

Smooth and uniform films (about 2 µm thickness) of poly(methyl methacrylate) (PMMA) containing 2 wt % biphenyl (BP) were spin coated on quartz plates and baked in vacuum to remove the residual solvent. BP was chosen as a dopant to induce the ablation efficiently.

An experimental setup is shown schematically in Fig. 1. A KrF excimer laser (248 nm, 30 ns FWHM) was used for inducing ablation and its intensity was adjusted by attenuation mirrors. The laser beam was focused to a small spot of about 0.1 cm² on a PMMA film surface at a slightly tilted angle. A Q-switched Nd³⁺:YAG laser (532 nm, 10 ns FWHM) was used as a probe light source of Michelson interferometer. The delay time between excitation and probe pulses was adjusted by a pulse generator and monitored with fast photodiodes and an oscilloscope. Time-resolved interference patterns were imaged by a CCD camera. All the measurements were performed at room temperature in air.

Michelson interferometer is in principle due to an inter-
ference between two beams, while it is here extended to three beams interferometry; two object and one reference beams. Two object beams are the reflections from the film surface and the back surface of the quartz plate. As a result of interference of the three beams, unique check-like images were obtained which are due to the superposition of three fringe patterns. Figures 2(a)–2(c) shows representative time-resolved interference images. In Fig. 2(a), two orthogonal counter patterns were superposed, where the longitudinal fringe generated by the interference of the reference beam with the reflected light from the film surface is ascribed to the surface profile, while the transverse one generated by the interference of two reflected beams from the film surface and the back surface of the quartz plate represents the distribution of the optical path length of the PMMA film and the quartz substrate. However, another pattern due to the interference of the reference beam and the reflected light from the back surface of the quartz plate cannot be seen, because of its low intensity.

Figure 2(b) shows an interference pattern at 200 ns after the laser irradiation ($\Delta t = \pm 200$ ns) at the fluence of 70 mJ/cm$^2$. The interrogated area was the same to that of Fig. 2(a). Deformation of longitudinal and transverse fringe patterns by excimer laser excitation was observed, which is interpreted as a film expansion and an increase of optical path length. The directions of the fringe movement for film expansion and increase in the optical path length were determined separately in the reference experiments. The interference pattern at the late stage ($t = \pm \infty$) is presented in Fig. 3(c), where the deformation of the fringe pattern disappeared completely and the initial pattern was recovered. Indeed no permanent etching was observed by the depth profiler except for the corner of the irradiated spot, which is due to the inhomogeneity by the high energy distribution of the excitation laser pattern.

The vertical resolution of this time-resolved interferometer is limited by the sinusoidal intensity distribution of fringe. A fringe displacement of about one-tenth of the fringe spacing can be resolved well, hence the detectable resolution of vertical height and optical path is about 30 nm. If the displacement of the polymer film during the probe pulse width is comparable to a half of wavelength of the probe laser, the former determines the vertical resolution. On the other hand, time resolution depends on the pulse width (10 ns) of the probe laser.

In the present work, we focus our attention to laser induced surface displacement of the polymer film, namely, morphological changes of expansion and contraction, and analyzed the movement of the longitudinal fringe. In Fig. 3, the surface displacement of 2 wt % BP-doped PMMA films are plotted against the laser fluence. Although the ablation threshold of 2 wt % BP-doped PMMA film is about 150 mJ/cm$^2$, transient expansion of the PMMA film was observed at the fluence of 65, 70, and 125 mJ/cm$^2$. The displacement of expansion of the polymer film was about 0.1–0.3 $\mu$m, which increased with the fluence. This transient expansion started within the excimer laser pulse ($\Delta t < +30$ ns), and the starting time became earlier with the fluence. When the fluence was 150 and 550 mJ/cm$^2$, we could not get clear fringe patterns at the stages later than 20 and 30 ns, respectively. This is because the expansion followed by ejection of ablated fragments was confirmed to be brought about, and removal of the ablated polymer distorted fringe patterns. The average expansion velocity of polymer films at the early stage can be estimated to be 45, 34, and 15 m/s for the fluence of 550, 150, and 125 mJ/cm$^2$, respectively.

At fluences lower than the threshold, the expansion continued longer than several milliseconds and disappeared slowly, and the initial surface was restored completely. When a neat PMMA film was used as a substance, a transient expansion was observed up to a few seconds. Since the thermal
The shift of Raman band due to PMMA ester side group and its polymer during this induction period.\textsuperscript{14,18} What happened in emission and absorption spectroscopy that doped molecules the molecular level, it was also shown by time-resolvedonds to break out morphological changes after excitation. At nanoseconds following laser irradiation. It has been consid-
ered that this method is a powerful tool for investigation of morphological dynamics undergoing laser ablation. Our results showed new features of laser ablation dynamics that surface expansion of the polymer film started during excimer laser pulse at an appreciable fluence and that the reversible contraction to the original flat surface in a few milliseconds, leaving no etching. These results indicate that morphological and molecular studies on laser ablation below threshold are important for understanding laser ablation dynamics and future application.

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