

M. HAUER
T. LIPPERT[✉]
A. WOKAUN

Nanosecond surface interferometry measurements on designed and commercial polymers

Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

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ABSTRACT The effect of the ablation mechanism on surface morphology changes during an ablation process was studied by comparing three different polymers: a triazene polymer, a polyimide and poly(methylmethacrylate) (PMMA) with nanosecond surface interferometry. The triazene polymer, for which only indications for a photochemical ablation mechanism had been detected in previous studies, revealed no surface swelling, which could be attributed to a thermal ablation mechanism. For polyimide, a photothermal ablation mechanism is usually used to describe the ablation process at irradiation wavelengths ≥ 248 nm. However, the interferometric measurements do not show any surface swelling, which would be a clear indication for a thermal ablation mechanism. A surface swelling was only detected for PMMA with irradiation at 248 nm and fluences below the threshold of permanent surface modification. The detected phase shift, which is proportional to the change of the film thickness and the refractive index, can be explained by the opposite signs of the thermal expansion coefficient and the thermal refractive-index coefficient.

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1 Introduction

Laser ablation is a promising tool to create microstructures in polymers. Due to several drawbacks (i.e. high ablation thresholds, low ablation rates, redeposition of debris) it is only used in a limited number of industrial applications (i.e. drilling of nozzles for ink-jet printers [1] and drilling of holes for multi-chip modules [2]). Various aspects of the ablation mechanism and laser processing in general are discussed in current reviews [3, 4]. It has been repeatedly emphasized that a better monitoring of the temporal evolution of the ablation process is important to understand the physical and chemical processes that characterize ablation. A more detailed understanding will help to improve the technique and to overcome some of the above-mentioned drawbacks. A variety of different time-resolved spectroscopy methods, such as absorption [5], emission [6, 7], infrared [8, 9] or Raman spectroscopy [10, 11], have been applied to probe the ablation process. Other techniques are used to analyze the ablation

products [12–15] or to measure the velocity of the shock wave released in air [16, 17].

In this study, nanosecond (ns) surface interferometry is used to observe the morphology changes of the polymer surface during the ablation process. A variation of this technique has been used in previous studies to observe the ablation process of different polymers. In some cases surface swelling prior to material removal was observed [18, 19], while in other cases the material removal started and ended with the laser pulse [19–21]. Pronounced surface swelling has been used as an indication for a photothermal process, where thermal expansion is observed prior to ablation.

Three polymers, i.e. a triazene polymer, a polyimide and poly(methylmethacrylate) (PMMA), were selected to study the influence of the ablation mechanism on the surface changes and to evaluate the appearance of different mechanisms in the interferometry. The triazene polymer belongs to a group of specially designed polymers with superior laser ablation properties (sharp ablation edges, no debris, low threshold fluence and high etch rates at low fluences [22]) and a high absorption coefficient at all applied wavelengths. Previous studies of this polymer gave indications for a photochemical ablation process at an irradiation wavelength of 308 nm [12]. It has been reported for KaptonTM, a polyimide which is very similar to the polyimide used in this study, that the irradiation wavelength has a pronounced influence on the ablation mechanism, i.e. photochemical at short wavelengths and photothermal at longer (≥ 248 nm) wavelengths [23]. Polyimide should therefore be a good example of a polymer where a transition from a photochemical to a photothermal ablation process can be observed. The polyimide and the triazene polymers are studied at three different irradiation wavelengths (193, 248 and 308 nm). The surface expansion of PMMA after 248-nm irradiation was studied as a reference for a clear thermal process at fluences below the threshold of permanent surface modification.

2 Experimental

The triazene polymer was prepared by a method described elsewhere [24]. The 1- to 2- μm -thick polymer films were spin coated from a chlorobenzene solution (10% polymer and 0.05% of a surfactant) of the polymer and dried for 24 h at 40 °C. The polyimide films (1–3 μm thickness)

✉ Fax: +41-56/310-2199, E-mail: thomas.lippert@psi.ch

were prepared by spin coating a precursor solution and baking the films for 1 h at 250 °C (under nitrogen atmosphere). It is noteworthy mentioning that this polymer is not identical with Kapton™, but it is the same polymer as used in another interferometric study [19]. The PMMA films were prepared by spin coating of a 15% solution of PMMA in chlorobenzene (with 0.05% surfactant) and drying the film in vacuum at 60 °C for 12 h.

The ns surface interferometry setup has been described in detail elsewhere [25]. Briefly, in a pump–probe setup an ArF (LPX 300, Lambda Physik, FWHM 25 ns), a KrF (LPX 100, Lambda Physik, FWHM 20 ns) or a XeCl (Compex 100, Lambda Physik, FWHM 30 ns) excimer laser was used to irradiate the polymer surface. The second harmonic of a Nd : YAG laser (Brilliant B, Quantel, FWHM 6 ns) was used in a Michelson interferometer to measure the thickness of the polymer film. To avoid the influence of the released shock wave on the interferometer, the thickness of the polymer was measured from the back side. Changes of the polymer thickness result in a change of the fringes from the Michelson interferometer. The data evaluation converts this fringe shift into a phase shift, which is proportional to the thickness change of the polymer film:

$$\Delta p(\Delta d) = 4\pi \frac{\Delta n_D}{\lambda} \Delta d. \quad (1)$$

From this equation the phase shift depends only on the change of the film thickness, Δd , the refractive index, n_D , and the wavelength, λ , of the probe beam. Within the same measurement series a linear relation between the ablation depth and the resulting phase shift is obtained, but the coefficient that relates both ((1) shows that this should only depend on λ and n_D , which are both constant) changes from measurement series to measurement series. Possible origins for this effect may be the multiple reflection of the laser beam within the thin film or slight changes of the angle of the substrate within the interferometer. At the moment, it is not clear which source is more important.

3 Results and discussion

3.1 Triazene polymer

The changes of the phase shift of the triazene polymer during and after irradiation with 193-, 248- and 308-nm laser light are shown in Fig. 1. The time $t = 0$ is defined as the time where the laser pulse starts (the laser intensity exceeds 1% of its maximum intensity). The positive phase shift corresponds to a decrease of the polymer thickness. The time profiles of the corresponding laser pulses and deposited energies are also included in Fig. 1. The scaling of the laser intensity and the deposited energy was adjusted to the beginning and the end of the phase shift of the polymer.

The changes of the surface morphology start and end with the laser pulse for all irradiation wavelengths and follow in all cases the deposited laser energy quite well. Small deviations are observed in the initial part of the deposited laser energy, i.e. slightly delayed for 248- and 308-nm irradiation and maybe faster for 193-nm irradiation. This behavior is also observed at other irradiation fluences (not shown) and is probably due to an ill-defined surface position (i.e. due to dense

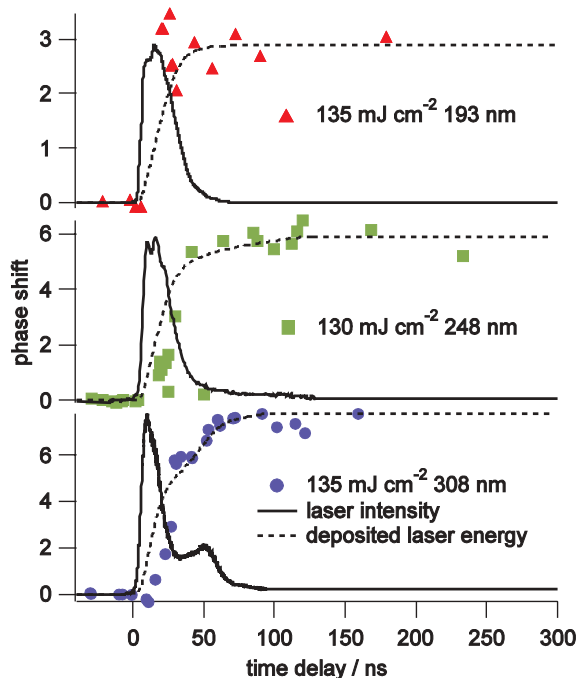


FIGURE 1 The phase shift versus time data of the triazene polymer surface during and after 193-, 248- and 308-nm irradiation. The laser intensities and the deposited energies are included in arbitrary units for each irradiation wavelength. The positive phase shift corresponds to ablation, i.e. surface removal

gaseous products) during the beginning of the ablation process. It is therefore not possible to attribute this delay directly to a delay in the surface-removal process.

The ablation of the polymer occurs without any sign of thermal expansion. This suggests that for all irradiation wavelengths a photochemical ablation mechanism is most important. This has also been supported by the detection of very similar ablation products for all irradiation wavelengths, which suggests identical reaction pathways, and the presence of excited nitrogen species that could not be explained by a thermal process [12].

3.2 Polyimide

The phase shift of the polyimide during and after irradiation at the three wavelengths is shown in Fig. 2. The laser intensity and the deposited energy are again included in the figure; the positive phase shift corresponds to material removal.

The changes of the phase shift occur at all wavelengths within the laser pulse. The changes of the phase shift for 193- and 248-nm irradiation are faster than the deposition of the pulse energy and are even more pronounced than in the case of the triazene polymer at 193 nm. For 308-nm irradiation the phase shift seems to follow the deposited energy quite well. As mentioned above it is not possible to relate this behavior directly to the material removal. However, it is apparent that the changes of the surface morphology are directly related to the length of the laser pulse (i.e. the 308-nm laser pulse has a long tail and surface changes are observed till the end of the laser pulse). No signs of a thermal swelling were detected, which

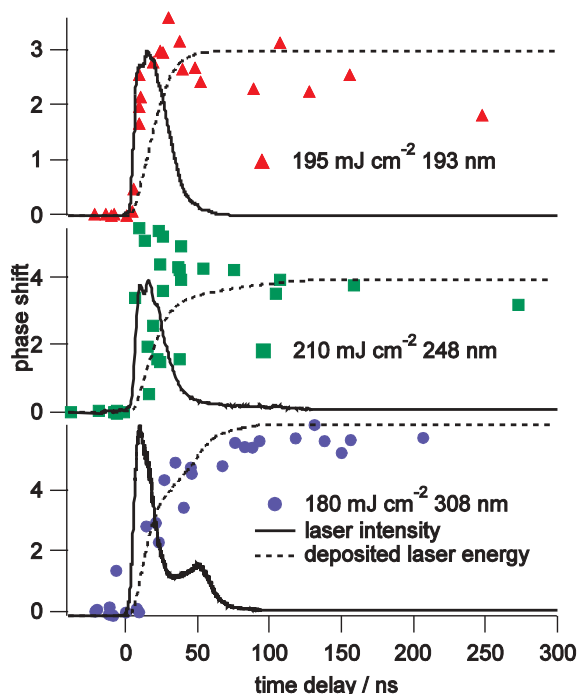


FIGURE 2 The phase shift versus time data of the polyimide surface during and after 193-, 248- and 308-nm irradiation. The laser intensities and the deposited energies are included in arbitrary units for each irradiation wavelength. The positive phase shift corresponds to ablation, i.e. surface removal

would be an indication of a photothermal ablation process of this polyimide.

For Kapton™ it is normally assumed that the ablation process at wavelengths ≥ 248 nm is mainly thermal [23]. Up to now only the polyimide used in this study was measured with interferometry. For an irradiation wavelength of 351 nm a thermal swelling prior to ablation was previously reported [19]. It seems that the ablation process changes significantly when the irradiation wavelength changes from 308 to 351 nm. The differences between the interferometric studies and other measurements may be caused by three different effects which can not be separated at the moment: the change of the dominant part in the mechanism from photochemical to photothermal is not observed between 193-nm and 248-nm irradiation, but between 308-nm and 351-nm irradiation; surface swelling is up to now only observed for polymers with a low absorption coefficient at the irradiation wavelength; the polyimide used in the interferometric studies has a different chemical structure and therefore different properties.

3.3 Poly(methylmethacrylate)

PMMA was applied as a reference polymer for a true thermal process. Irradiation below the threshold of permanent surface modifications (i.e. reactions) should only be due to thermal heating of the polymer. PMMA exhibits a quite high threshold of permanent surface modifications at an irradiation wavelength of 248 nm (900 mJ cm^{-2} , ablation threshold 1400 mJ cm^{-2} [21]).

The phase changes of the PMMA film after 380 mJ cm^{-2} at an irradiation wavelength of 248 nm are shown in Fig. 3. The laser intensity and the deposited laser energy are also in-

cluded in the graph. The positive phase shift in this graph now represents a surface expansion. The transient expansion of the polymer starts with the laser pulse and is observed for more than $10 \mu\text{s}$. Images taken several seconds after the laser pulse do not reveal a permanent swelling of the polymer surface. An oscillatory behavior of the polymer surface after irradiation at 248 nm has also been reported [21] and was attributed to transitions over the glass-transition temperature T_g of the PMMA. Our measurements do not reveal such an oscillatory behavior, and we suggest that the observed variations are most likely due to noise in the measurements related to the small phase shifts.

There is one experimental difference between the measurements reported earlier [21] and those reported in this paper. Our measurements are performed with the probe beam coming from the back side of the polymer, while the measurements of Masabuchi et al. [21] were performed from the front side of the polymer. Our measurements are influenced by the index of refraction of the polymer, which changes with temperature. The change of the index of refraction with temperature ($T < T_g$: $dn/dT = -1.1 \times 10^{-4} \text{ K}^{-1}$, $T > T_g$: $dn/dT = -2.1 \times 10^{-4} \text{ K}^{-1}$) [26] has the same order of magnitude as the expansion coefficient of the polymer ($T < T_g$: $dn/dT = 2.4\text{--}2.7 \times 10^{-4} \text{ K}^{-1}$, $T > T_g$: $dn/dT = 5.6\text{--}5.8 \times 10^{-4} \text{ K}^{-1}$) [26], but with the opposite sign. This results in the effect that both effects counteract each other, resulting in a small change of the phase and only minor changes when the temperature exceeds T_g . We were therefore not able to detect the previously described oscillations.

PMMA has a low absorption coefficient at 248 nm and also reveals a high threshold of permanent surface modifications. It noteworthy that the counteracting effect of the thermal expansion and the temperature change of the refractive index can be rationalized with the temperature-dependent values that have been obtained for low heating rates. In the case of the interferometric studies, heating rates of up to $2.5 \times 10^9 \text{ K s}^{-1}$ are obtained, and it has always been a matter

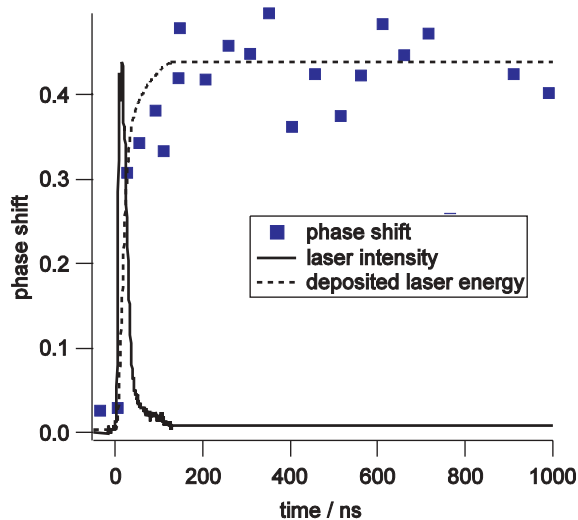


FIGURE 3 The phase shift versus time data of PMMA during and after irradiation with 380 mJ cm^{-2} at 248 nm. The laser intensity and the deposited energy are included in arbitrary units. The positive phase shift corresponds to a surface expansion

of discussion whether these reference values will also hold for high heating rates. Our studies suggest that this may be the case, which has also been observed by Masabuchi et al. [21].

It is also interesting to emphasize that PMMA has at 248 nm a very low absorption coefficient ($< 200 \text{ cm}^{-1}$), which supports the suggestion above that expansion is observed for polymers with low absorption coefficients at the irradiation wavelength. The correlation of the absorption coefficient with material properties such as thermal expansion is an interesting tool for further modeling.

4 Conclusion

The measurements of the different polymers reveal a clear influence of the ablation mechanism on the time-resolved surface changes of the polymer. The triazene polymer reveals no surface swelling, which would be an indicator for a thermal process, after laser irradiation at different wavelengths with fluences above the ablation threshold. This is in agreement with previous studies of the triazene polymer, where mainly indications for a photochemical ablation process were found.

A transition from a photochemical to a photothermal ablation mechanism was expected to be observed for polyimide, but the results reveal no indication of a photothermal ablation mechanism at irradiation wavelengths of 248 or 308 nm. Whether this result is due to the different chemical structures of the polyimide of this study and KaptonTM, for which a photothermal ablation mechanism has been assigned for wavelengths $\geq 248 \text{ nm}$, or if thermal expansion is only observed for polymers with a low expansion coefficient at the irradiation wavelengths, is the subject of an ongoing study.

A surface swelling was detected for PMMA with irradiation at 248 nm and fluences below the threshold of permanent surface modification. The detected small phase shift can be explained by the opposite signs of the thermal expansion coefficient and the thermal refractive-index coefficient. This suggests that these indices, obtained at low heating rates, behave similarly at high heating rates ($2.5 \times 10^9 \text{ K s}^{-1}$).

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