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Femtosecond laser-induced decomposition in triazenepolymer thin films

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Abstract

The damage induced by ultrashort, 130 fs, near-infrared, 800 nm, Ti:sapphire laser pulses in 1 μm thick triazenepolymer films on glass substrates has been investigated. Real-time reflectivity measurements with a ps-resolution streak camera and a ns-resolution photodiode set-up have been performed to study in situ the structural transformation dynamics upon single-pulse excitation with laser fluences above the threshold of permanent damage. Scanning force microscopy has been used to probe ex situ the corresponding surface topography of the ablated spots. Modulated lateral force microscopy (M-LFM) has been applied to observe alterations of the local friction properties within and around the irradiated areas.

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1. Introduction

For more than two decades, the laser processing of polymers has been intensively studied, especially in the UV regime where many polymers of interest are highly absorbing [1–4]. One polymer group of particular interest is that of the triazenepolymers [5] which are photochemically very active upon UV irradiation and have superior ablation properties by irradiation at $\lambda = 308$ nm [6].

In a previous study [7], we have investigated the behaviour of a triazenepolymer film upon irradiation with single ultrashort near-infrared, 800 nm, pulses that, due to their high intensities, may be an alternative way of structuring by means of multi-photon absorption in the material. That work mainly focused

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on determining the physical mechanisms which apply during the irradiation with pulse durations varying between 130 fs and 2.6 ps and at fluences below and slightly above the damage threshold fluence of 495 mJ/cm^2. A model based on optical interference effects was proposed to explain the observed transient probe reflectivity changes, caused by the decomposition of the polymer within the film material. It was suggested that in this intensity regime of 10^{11} to 10^{13} W/cm^2, the damage is mainly caused by linear absorption effects either at absorbing inhomogenities, which tend to pile up at the film interfaces, or within the polymeric material itself via free-carrier absorption with subsequent avalanche-ionisation.

In the study reported here, we extend our previous work by investigating higher fluences and by the use of scanning force microscopy (SFM) and modulated lateral force microscopy (M-LFM) techniques. These techniques analyse the surface morphologies and alterations and allow a quantitative visualisation of the material removal to be made. New evidence is presented to suggest that the film damage is not just caused by a surface ablation mechanism.

2. Experimental

The polymer film, with the chemical structure shown in Fig. 1a, has been synthesised according to a procedure described in Ref. [8]. The samples for the experiments have been prepared on glass substrates by solvent casting or spin coating of a 10 wt.% solution of the polymer in a 1:1 mixture of cyclohexanone/chlorobenzene with one additional drop of a surfactant, Pluronic L-62, resulting in a final film thickness of about 1 μm.

A commercial chirped pulse amplification (CPA) Ti:sapphire laser system (Spectra Physics, Spitfire), providing linearly polarised pulses of 130 fs duration at $\lambda = 800$ nm, was used for irradiation. The polymer film is essentially transparent at the irradiation wavelength having a photon energy of 1.55 eV such that, in the linear absorption regime at low intensities, the optical penetration depth $1/\alpha$ exceeds the film thickness by several orders of magnitude.

In the irradiation set-up, the sample was placed at normal incidence close to the focal plane of a lens with 150 mm focal length, resulting in an almost circular laser spot on the surface that corresponds approximately to a spatial Gaussian distribution with a $1/e^2$-diameter of about 100 μm. An *xyz*-translation stage was used for precise re-positioning of the sample to a new location after each single pulse irradiation in air.

The temporal evolution of the surface reflectivity upon irradiation has been monitored using a single mode Ar^+ laser operating at $\lambda = 514.5$ nm. This probe beam was focused at the centre of the fs-laser irradiated region to a spot diameter, $1/e^2$, of about 30 μm, at an angle of incidence of 18°. The intensity evolution of the reflected probe beam was then recorded by a streak camera (Hamamatsu Model C5680), equipped with a single sweep unit Model M5676 providing a time-resolution of 350 ps in a time window of 50 ns and by a photodiode/oscilloscope detection system with several ns temporal resolution. More details regarding this real-time reflectivity (RTR) measurements set-up are described in Ref. [9].

SFM in the contact mode has been used to probe the surface topography of the laser irradiated spots with a high lateral and vertical precision in the nm range. The basic instrumentation of the employed scanning force microscope (type "Explorer") was supplied by Thermo-Microscopes/TopoMetrix.

M-LFM [10] has been applied to visualise alterations of the local friction properties within and around the irradiated areas (modulation amplitude < 5 nm at a frequency of 66 kHz).

3. Results and discussion

At fluences exceeding the single pulse damage threshold of the triazenepolymer film, 495 mJ/cm^2 [7], the RTR set-up has been used to study the transient surface reflectivity for three different laser fluences of 495, 1020, and 1940 mJ/cm^2. Fig. 1 shows the normalised reflectivity as measured with the streak camera in a 50 ns time window (see Fig. 1b, f, and j), and simultaneously recorded with the photodiode detection system on a timescale up to 1.5 μs after the irradiation (see Fig. 1c, g, and k).

At a fluence slightly above the damage threshold, the reflectivity shows a sharp temporal drop, followed by rapid oscillations with a normalised amplitude around 0.75 lasting for a few nanoseconds (see Fig. 1b). This behaviour is consistent with the

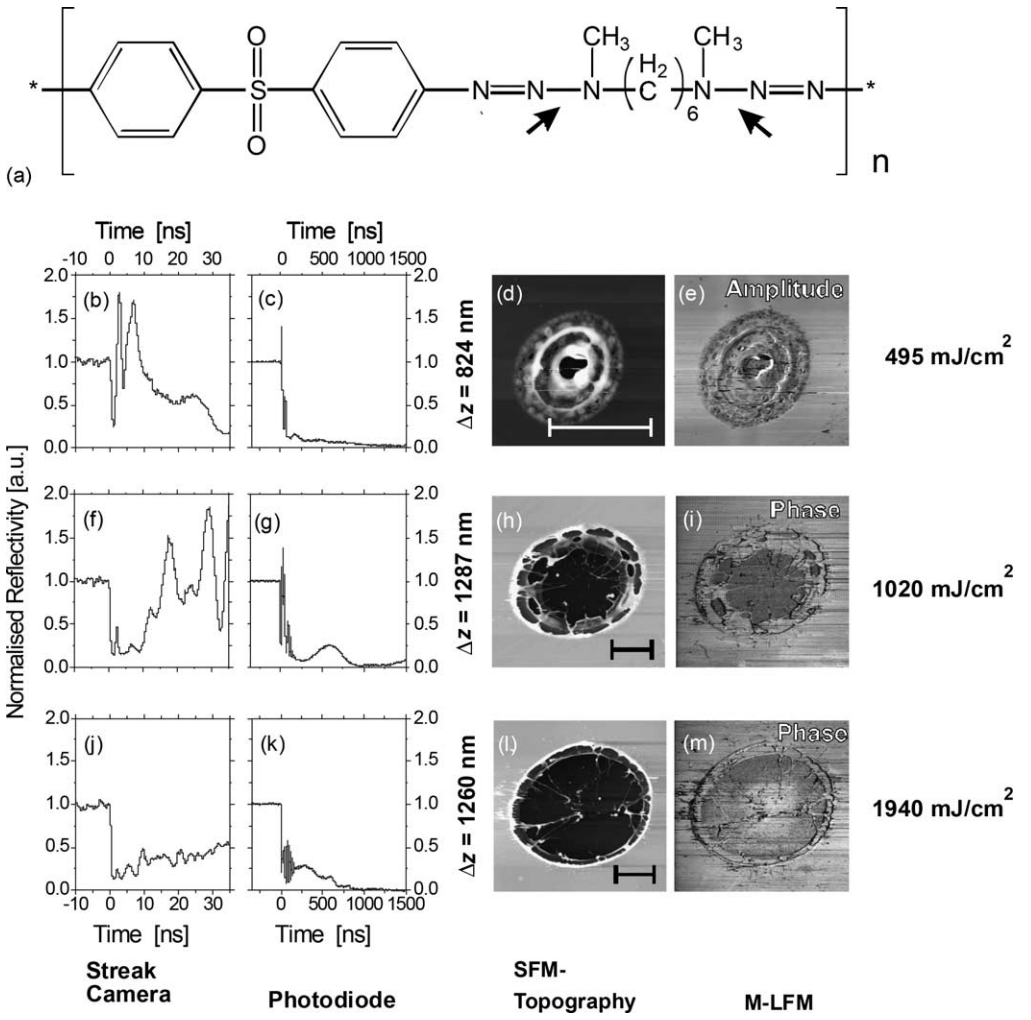

Fig. 1. Chemical structure of the triazenepolymer (a) where arrows indicate the weakest bonds. Normalised reflectivity and microscopy images of the polymer film on glass after irradiation with single 130 fs laser pulses at three different fluences above the damage threshold [(b)–(e): 495 mJ/cm^2, (f)–(i): 1020 mJ/cm^2, (j)–(m): 1940 mJ/cm^2]. Reflectivity transients measured simultaneously with the streak camera [(b), (f), and (j)] and photodiode [(c), (g), and (k)] are shown. SFM topography images with a 30 μm scale bar are shown in (d), (h), and (l) with the maximum height difference (Δz) displayed on the left hand side of each image. In (e), the simultaneously acquired M-LFM amplitude signal image is shown, whereas (i) and (m) show M-LFM phase signal images.

formation of gas bubbles inside the film due to the decomposition of the polymer into gaseous components. Assuming that the polymer decomposition starts at the weakest N–N bonds, marked by arrows in Fig. 1a, gaseous N_2 is created as the primary decomposition product [7]. Optical simulations of thin polymer films on a glass substrate (not shown here) indicate that a decrease of the film refractive index n would cause a decrease of its reflectivity. The initial reflectivity drop in Fig. 1b can thus be related to a decrease of the effective refractive index caused by the formation of gas in the polymer matrix. The reflectivity oscillations would then arise from interference effects at the gas/polymer interfaces as the bubbles expand. Dijkkamp et al. have shown that gas bubbles can be formed at the polymer/substrate interface upon laser irradiation of non-absorbing polymer films on absorbing substrates [11]. On longer

timescales, after the initial reflectivity oscillations are terminated, a significant decrease of the reflectivity can be observed, see Fig. 1c. Permanent film damage has been observed after the irradiation at that fluence level of 495 mJ/cm^2.

A very similar but more complicated behaviour of the reflectivity transient can be observed for higher laser fluences exceeding the damage threshold more than twice. However, the onset of the characteristic reflectivity oscillations after the initial reflectivity decrease is delayed when increasing the laser fluence to values of 1020 mJ/cm^2 (see Fig. 1f and g), and 1940 mJ/cm^2 (see Fig. 1j and k).

Additionally, the three optically probed damage spots have been subjected to ex situ SFM investigations employing the M-LFM technique. Fig. 1d, h, and l show the corresponding greyscale encoded SFM topography images, whereas Fig. 1e shows the M-LFM amplitude signal. Figs. 1i and m display the M-LFM phase signal images. At the lowest fluence of 495 mJ/cm^2, the SFM topography, Fig. 1d, shows a permanent material modification area with a diameter of 33 μm. This modification obviously causes a swelling of the polymer material which results in the formation of a mound around a topographically lower area with a diameter of 18 μm. This mound circumvents a significantly smaller ablation crater with an inner diameter of 8 μm. The corresponding M-LFM amplitude image reveals a reduced amplitude signal in the entire modified area (see Fig. 1e). At a higher fluence of 1020 mJ/cm^2, a much larger crater with a diameter of 95 μm is seen in Fig. 1h. Also, some redeposited polymeric filaments are visible within the ablated area. These are indicative of a bubble which has evolved in the film and collapsed during the ablation process. Within the regions where most of the polymer film has been removed, the surface also exhibits a reduced M-LFM phase signal such as in the image of Fig. 1i. A similar behaviour can be seen even at a higher fluence of 1940 mJ/cm^2 in the topography image shown in Fig. 1l and the in the M-LFM phase signal image in Fig. 1m. The M-LFM also indicates that the material modification, which is associated with the laser-induced swelling of the polymer, simultaneously causes an alteration of the friction coefficient of the surface as evidenced by comparing Fig. 1d and e. Furthermore, the areas where most of the film has been removed also exhibit a modified friction coefficient, compare Fig. 1h and i. Most probably these modifications arise from chemical alterations of the polymer due to the fs laser pulse irradiation, such as a fractioning of the polymer chains, carbonisation, and oxidation.

To analyse the laser-induced damage process of the polymer film quantitatively, the SFM topography images of the spots irradiated with various fluences have been used to determine diameters of the modified areas (D) and the maximum crater depths (h). The modification diameters have been evaluated instead of the ablation diameters since they are more accurately determined by SFM due to the redeposition of polymeric material in the regions of the crater wall. Furthermore, since the laser-modified areas were not perfectly circular, the modifications diameters have been characterised by values of the long and perpendicular short axis diameters D_x and D_y, respectively. In the case of single-pulse surface ablation with a spatial Gaussian beam, the crater depth scales with the logarithm of the incident fluence, i.e.:

$$h = \kappa \ln\left(\frac{\phi_0}{\phi_{\mathrm{abl}}}\right), \tag{1}$$

where κ is a proportionality constant which depends on the material and the irradiation conditions, and ϕ_0 and ϕ_{abl} are the laser peak fluence and the ablation threshold fluence, respectively [4]. This model of surface generated damage has been successfully applied for the analysis of the modification and ablation of a variety of bulk polymers with near-IR fs laser pulses [12–14]. For the product of the surface modification diameters, a similar logarithmic scaling law was found [12,15] which is generalized here in order to consider the non-circularity of the spatial beam profile by

$$D_x D_y = 2 w_{0,x} w_{0,y} \ln\left(\frac{\phi_0}{\phi_{\mathrm{mod}}}\right), \tag{2}$$

where $w_{0,x}$ and $w_{0,y}$ are the Gaussian $1/e^2$-beam radii in the x- and y-directions, respectively, and ϕ_{mod} is the threshold fluence for the irreversible modification $\phi_{\mathrm{mod}} < \phi_{\mathrm{abl}}$. Combining both Eqs. (1) and (2) leads to an expression that relates the ablation crater depths to the modification diameters via

$$h = A(D_x D_y) - C. \tag{3}$$

Here, the proportionality constant is

$$A = \frac{\kappa}{2w_{0,x}w_{0,y}} \tag{4}$$

and

$$C = \kappa \ln\left(\frac{\phi_{\mathrm{abl}}}{\phi_{\mathrm{mod}}}\right) > 0 \tag{5}$$

is an offset constant.

Fig. 2 shows the experimental data of the maximum crater depth h as function of the modification diameter product D_xD_y obtained from the SFM topography images. The experimentally determined crater depths show a distinct step-like behaviour with a saturation value of 890 nm. This value is slightly smaller than the polymer film thickness of 1 μm, measured by SFM at a mechanically induced scratch at another location on the film. The observation that there is always a residual organic film left covering the glass substrate surface after the intense laser ablation has been further confirmed by high-resolution SFM images (not shown here) and provides further evidence of the importance of the gas bubble formation within the film [7]. This is seen in Fig. 2 where the experimental data upon fs laser ablation of the triazenepolymer film are clearly not consistent with a surface ablation model which predicts a linear relationship between the crater depths h and the modification diameter products D_xD_y as seen in Eq. (3). It may be expected that redeposited material

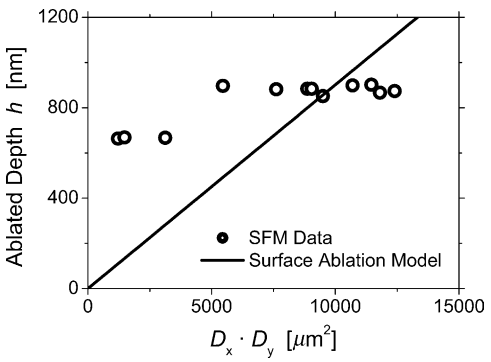

Fig. 2. Maximum crater depth h in an 1 μm thick triazenepolymer film as function of the product of the modification diameters D_xD_y after irradiation with single near-IR laser pulses of 130 fs duration. Open circles: data from SFM evaluation. Solid line: least-squares-fit of the surface ablation model to the experimental data using to Eq. (3).

caused by the evaporation of polymeric material also contributes to the residual organic film in the crater in addition to the filament formation described previously. However, this redeposition scenario is rather unlikely since this latter process depends smoothly on the laser fluence [16] in contrast to the observed step-profile in the crater depth as a function of fluence. Furthermore, the depth of each observed step is 230 nm which agrees very well with the spatial distance $\lambda/(2n_{\mathrm{Polymer}})$ of the consecutive interference maxima of a standing wave within the film material. These maxima are generated from partial reflections of the fs-pulse at the air/polymer and the polymer/glass interface (wavelength $\lambda = 800$ nm, refractive index $n_{\mathrm{Polymer}} = 1.6$–$1.8$). This experimental fact also supports the interference-based damage mechanism proposed in Ref. [7].

4. Conclusions

The damage of triazenepolymer films on glass substrates upon irradiation with single near-infrared ultrashort laser pulses at $\lambda = 800$ nm and with a pulse duration of 130 fs have been investigated by means of in situ RTR measurements and ex situ SFM and modulated lateral force microscopy. Our complementary RTR and microscopy results give evidence that the damage process of the polymer films is associated with the formation, growth and collapse of gas bubbles within the film. This is supported by three experimental observations: (i) the occurrence of reflectivity oscillations on the ns timescale, (ii) the redeposition of non-ablated bubble fragments forming an annular structure or filaments at the crater walls, and (iii) a scaling behaviour of the ablation depth and modification diameters which is not consistent with basic models of surface ablation. Even at the highest fluences of fives times the damage threshold fluence it was not possible to completely remove the organic film from the underlying glass substrate. An analysis of the crater depth strongly supports the interference based damage mechanism within the film material. Based on our results, the structuring of thin triazenepolymer films with near-IR ultrashort laser pulses of 100 fs duration is not a suitable alternative for UV ablation.

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