

Laser-induced ablation dynamics and flight of thin polymer films

P. Frank · J. Shaw-Stewart · T. Lippert · J. Boneberg ·
P. Leiderer

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Abstract We investigated the ejection dynamics of triazene polymer layers in the thickness range of 40 nm to 600 nm upon nanosecond laser ablation at a wavelength of 532 nm. The ablation is due to laser-induced thermal degradation of a small part of the polymer in contact with the silicon substrate. The subsequent dynamics of the flying polymer layer are measured with sub-nanosecond time resolution. The evaluation of the initial velocity for different film thicknesses gives insight into the energy transfer process during the acceleration of the films.

1 Introduction

Photolabile polymers with an aryl-triazene unit in the backbone were first synthesized in the early 1990s, for the purpose of laser ablation [1]. Throughout the last decade, research into triazene polymers (TP) has been revived as it has found an application as a dynamic release layer (DRL) for laser-induced forward transfer (LIFT) [2]. The polymers have originally been tailored for the use of a 308 nm excimer laser. The dynamics of the ablation by UV lasers have been investigated in great detail [3–5], including shadowgraphic

imaging of the triazene flyer [6, 7]. The theoretical ablation mechanism for TP is not fully understood, but it is known to have a significant photochemical element [8]. In general, however, ablation is dominated by thermal factors, and even for TP an ablation model based exclusively on thermal factors has been demonstrated [9].

Reflectometric measurements give the possibility to detect the movement of ablated films with high temporal and high vertical resolution. This has been demonstrated by the in-depth study of the thermal ablation process of liquid films [10, 11] and of solid CO₂ films [12]. Therefore, the investigation of triazene polymer ablation with high-resolution reflectometry should give further insight into the ablation dynamics of thin triazene films.

2 Experimental setup

The setup for detecting the laser ablation of triazene layers consists of a fast reflectometer (cw laser diode, $\lambda = 660$ nm) with high temporal (below 1 ns) and spatial resolution in vertical direction (<10 nm) [13]. The triazene polymer used is synthesized according to the process described for TP-6a in [14]. It is spin-coated from a cyclohexanone:chlorobenzene (1:1) solution onto clean silicon substrates. The thickness of the layer is changed by varying the TP solution concentration and spin speed. It is measured with a profilometer. Six different thicknesses between 40 ± 5 nm and 595 ± 5 nm have been used. The refractive index of the triazene polymer at the used wavelength of 532 nm has been determined to $n = 1.65 \pm 0.05$ by an ellipsometric measurement.

The ablation is initiated by a focused Nd:YAG laser pulse ($\lambda = 532$ nm, FWHM = 10 ns) with nearly orthogonal incidence ($\approx 80^\circ$). The pulse energy is monitored with a thermal energy detector.

P. Frank (✉) · J. Boneberg · P. Leiderer
University of Konstanz, 78457 Konstanz, Germany
e-mail: Pascal.Frank@uni-konstanz.de

J. Shaw-Stewart
EMPA, Swiss Federal Laboratories for Material Testing and Research, Laboratory for Functional Polymers, Überlandstrasse 129, 8600 Dübendorf, Switzerland

J. Shaw-Stewart · T. Lippert
General Energy Research Department, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

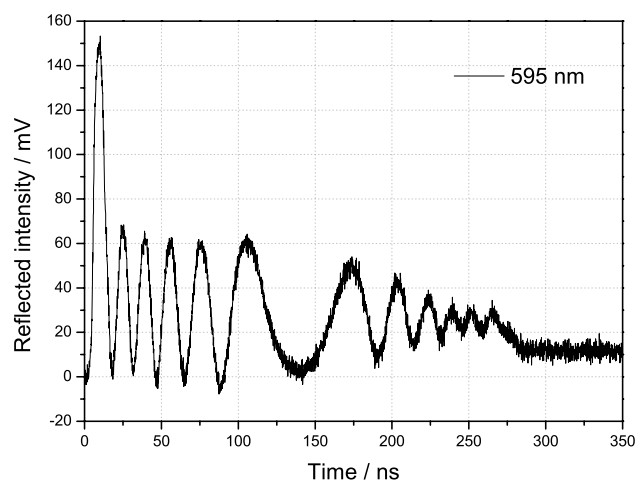


Fig. 1 Reflected intensity of a 595 nm thick triazene layer flying from a silicon substrate after laser ablation

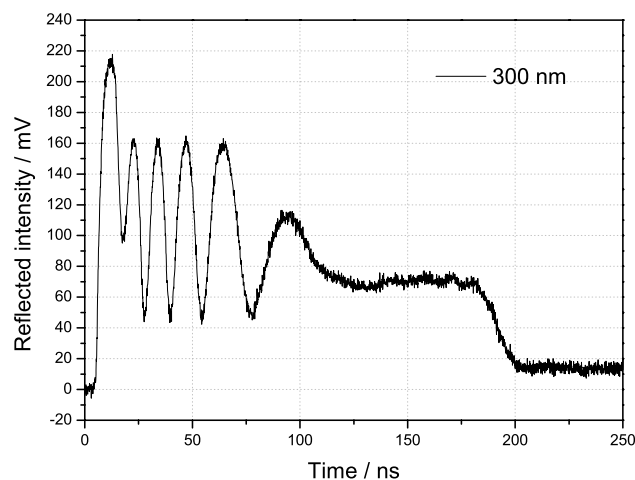


Fig. 2 Reflected intensity of a 300 nm thick triazene layer after laser ablation

3 Results

Typical signals of the fast reflectometer for the ablation of the triazene polymer with two different layer thicknesses are shown in Figs. 1 and 2. The incident energy density is about 30% above the melting threshold of silicon. The first dominant peak is therefore due to the enhanced reflectivity of molten silicon [15]. The resolidification takes place on the order of ten nanoseconds. The signal of the triazene flyer in this time period is not substantially disturbed. The signal of a 595 nm thick TP film in Fig. 1 shows oscillations in the reflected intensity which slow down for about 150 ns. Then the oscillations speed up again and after 290 ns the signal drops back to a constant value. The signal for the thinner film (300 nm, Fig. 2) starts qualitatively similar, but lacks pronounced features past 100 ns. It drops back to a near initial value after 200 ns. The descent is smeared out over 20 ns.

4 Discussion

The signals in Figs. 1 and 2 reflect the flight of the TP layer after ablation from the silicon substrate and back. The laser pulse heats the silicon substrate well above the thermal degradation temperature of the TP, which starts at 500 K for quasistatic heating [1]. The threshold fluence for TP ablation at the used laser parameters is around 70% of the melting threshold of silicon. In comparison with the melting temperature of silicon (1685 K), the actual ablation temperature is in the order of reported values with comparable heating rates (≈ 1450 K, [9]). The heat then diffuses into the first few nanometers of the polymer, which then degrade and form a layer of the degradation products of the polymer. Since most

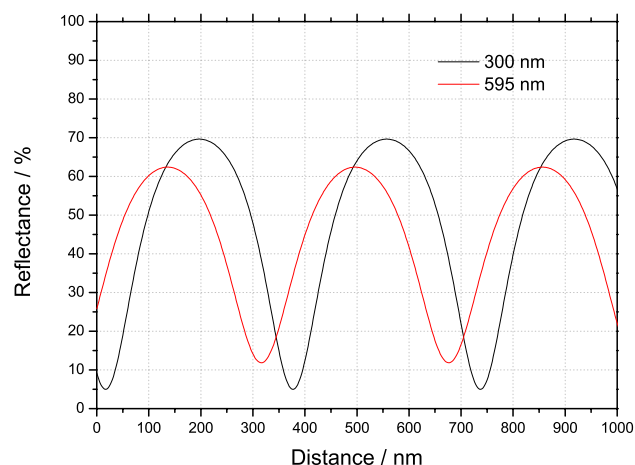


Fig. 3 Calculated reflectance of the system consisting of a TP layer of given thickness, a gaseous layer of variable thickness and the silicon substrate

of these products are gaseous, this layer is at elevated pressure [16]. The overlying polymer layer is therefore accelerated from the substrate. The reaction kinetics of the degradation process taking place at the very beginning of the flight is too fast to be resolved with the experimental setup. In addition, it is obscured by the prominent signal of the melting silicon. The interference of the reflections of the detecting laser beam from the moving TP layer and the silicon substrate is used to detect the distance between the layer and the substrate. Figure 3 shows the calculated reflectivity of a multilayer system consisting of a TP layer of given thickness, a gaseous layer of variable thickness, and the silicon substrate. By comparing the calculated values to the experimental signals, it is feasible to get access to the full information on the trajectory of the flight of the layer. Thus, the varying oscillation frequency of the signals in Fig. 1 can be explained. As the period decreases, the flyer slows down with increasing

distance to the silicon substrates. It stops at 150 ns, which corresponds to a distance of 2.1 μm , and is pushed back to the substrate afterward. This is alleageable if one takes into account that the experiments are done under ambient conditions. The kinetic energy of the flyer at its maximal value after leaving the substrate is therefore transformed into potential energy in a pressure difference, as the pressure underneath the films drops below the ambient value. This accelerates the film back toward the substrate. The return is only possible, if the pressure difference can build up and is not diminished by gas flow through holes or from the surrounding. It would not be observable if the film broke up into small fragments. The minimal lateral dimension of such fragments is determined by the speed of the gas, flowing around the edges of the fragments. Assuming this will not be faster than the speed of sound, the minimal value is a few 100 micron. However, different fragment sizes within the focal spot of the detecting laser (about 200 microns) will lead to velocity differences. These result in a distance inaccuracy which smears out the distinct interference of the reflected beams. This could be the reason for the fading of the signal intensity on both signals, which is, however, very prominent at the data of the 300 nm thick TP layer in Fig. 2. A lateral displacement of around 150 nm leads to almost complete distinction of the information, so only weak interference is observable. The return of the different fragments to the silicon substrate is therefore not simultaneous, but staggered.

The considerations about the 6 flight trajectory due to the pressure differences are analogous to a detailed model in [10], which describes the flight of *fluid* films. The model is based on the assumption that the potential energy, which is kept in the gas cushion with elevated pressure after the degradation, is transformed into kinetic energy of the film. After a certain distance (a couple of 100 nm, depending on the generated pressure and the amount of transformed material) the pressure equals ambient pressure. At this point, 30 to 50 ns after the lift-off of the layer, all energy is transferred into kinetic energy. Subsequently, the pressure underneath the film drops below values of the pressure above it, which is nearly constant at ambient pressure since the velocity of the flyer is distinctly below the velocity of sound in air. The initial velocities are extracted for TP layers in the thickness range between 40 nm and 600 nm, and are shown in Figs. 4 and 5. Figure 4 shows the data as function of the incident laser energy. The velocity increases by less than 15% when the incident energy is doubled. A close consideration of the energy dependence would have to be based on the dissipated energy, which is depending on the temperature of the substrate and the actual ablation time after the onset of the laser pulse. This demands an accurate temperature simulation and measurement of the ablation time in the sub-nanosecond regime, as the heating rate during the laser pulse is very high. As most of the measurements are

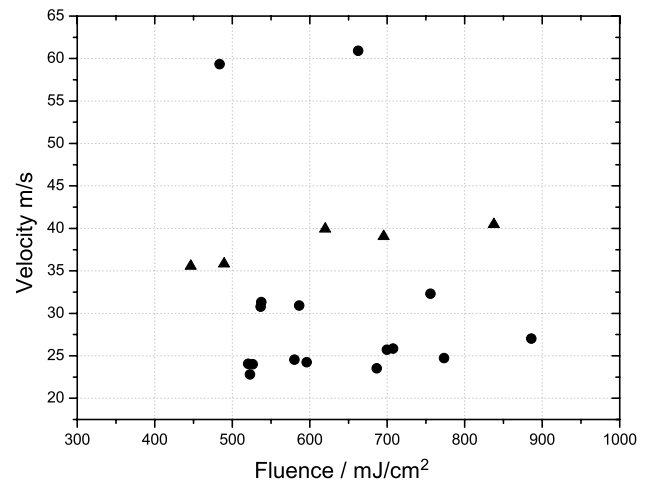


Fig. 4 Maximal velocity of TP layers with thicknesses between 105 nm and 595 nm depending on the incident laser fluence. The *triangles* mark the velocities of 184 nm thick films

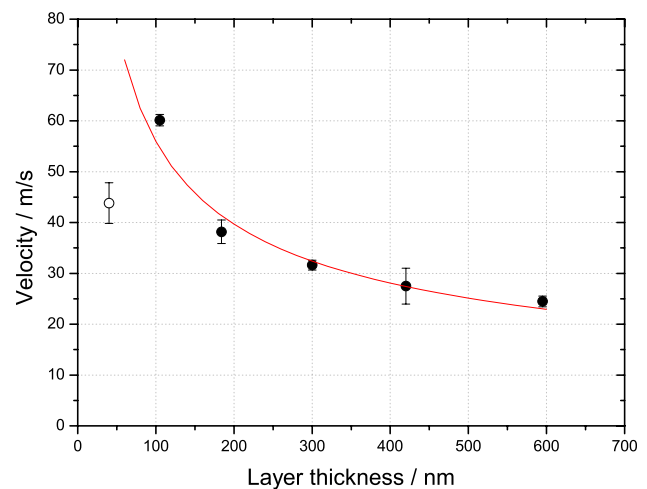


Fig. 5 Velocity of 40 nm to 595 nm thick TP films. The *red line* indicates a power law fit to the filled data points with exponent $m = -0.5$

done above the silicon melting threshold, the determination of the ablation time is not feasible. It is nevertheless obvious that the dependence of the velocity on the TP layer thickness is significant (see Fig. 5). The velocity is about 60 m/s for thin (105 nm) layers and decreases to 25 m/s for thicker (595 nm) layers. The value for the thinnest examined films (40 nm) contradicts this trend, but the signals of these films do not display well-defined characteristics. The ablation of these thin films is most probably not homogeneous and a rupture of these films is likely to occur. Thus, the pressure is not completely transferred into kinetic energy.

The kinetic energy E depends on the velocity v , on the layer thickness d and the density ρ . Per unit area it is: $E = \frac{1}{2} \rho d v^2$. Hence, constant kinetic energy leads to $v \propto d^{-0.5}$. This dependence is indicated in Fig. 5 by the red line which fits the data for films thicker than 100 nm. The kinetic en-

ergy of the different films is almost equal. The assumption of a thickness-independent transfer process of energy is therefore justified.

5 Conclusion

The flight of thin layers of triazene polymers has been investigated after laser-induced ablation from a silicon substrate. Under sufficiently homogeneous conditions, the layers return to the substrate after some hundred nanoseconds. The maximum distance of the flyers to the substrate is in the range of a few microns. The initial velocity of the films, extracted from the trajectories, determines their maximum kinetic energy. In comparison to previous studies on different materials, namely liquid isopropanol and solid microporous CO₂ layers [11], the TP shows a thickness-independent kinetic energy as seen for fluid films. The CO₂ films reveal an additional dissipation mechanism, which is due to its porosity, but not understood in detail yet. The TP films are solid, also, but have a porosity which is at least one order of magnitude less than the CO₂ films. Hence, their behavior is directly comparable to that of the intact liquid isopropanol films. The considerations of the flight of thin polymer films, therefore, contribute substantially to the general understanding of the flight of thin films after laser ablation.

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References

1. T. Lippert, A. Wokaun, J. Stebani, O. Nuyken, J. Ihlemann, *Angew. Makromol. Chem.* **206**, 97–110 (1993)
2. A. Doraiswamy, R.J. Narayan, T. Lippert, L. Urech, A. Wokaun, M. Nagel, B. Hopp, M. Dinescu, R. Modi, R.C.Y. Auyeung, D.B. Chrisey, *Appl. Surf. Sci.* **252**, 4743–4747 (2006)
3. T. Lippert, J. Stebani, J. Ihlemann, O. Nuyken, A. Wokaun, *J. Phys. Chem.* **97**, 12296–12301 (1993)
4. L.S. Bennett, T. Lippert, H. Furutani, H. Fukumura, H. Masuhara, *Appl. Phys. A* **63**, 327–332 (1996)
5. R. Fardel, P. Feurer, T. Lippert, M. Nagel, F.A. Nüesch, A. Wokaun, *Appl. Surf. Sci.* **254**, 1332–1337 (2007)
6. R. Fardel, M. Nagel, F. Nüesch, T. Lippert, A. Wokaun, *J. Phys. Chem. C* **113**, 11628–11633 (2009)
7. R. Fardel, M. Nagel, F. Nüesch, T. Lippert, A. Wokaun, *J. Phys. Chem. C* **114**, 5617–5636 (2010)
8. T. Lippert, M. Hauer, C.R. Phipps, A. Wokaun, *Appl. Phys. A* **77**, 259–264 (2003)
9. R. Fardel, M. Nagel, T. Lippert, F. Nüesch, A. Wokaun, B.S. Luk'yanchuk, *Appl. Phys. A* **90**, 661–667 (2008)
10. F. Lang, P. Leiderer, *New J. Phys.* **8**, 14 (2006)
11. P. Frank, J. Graf, F. Lang, J. Boneberg, P. Leiderer, *Appl. Phys. A* **101**, 1–5 (2010)
12. J. Graf, B. Luk'yanchuk, M. Mosbacher, M.H. Hong, C.T. Chong, J. Boneberg, P. Leiderer, *Appl. Phys. A* **88**, 227–230 (2007)
13. F. Lang, Ph.D. Thesis, University of Konstanz, 2007
14. M. Nagel, R. Hany, T. Lippert, M. Molberg, F.A. Nüesch, D. Rentsch, *Macromol. Chem. Phys.* **208**, 277–286 (2007)
15. D.H. Auston, J.A. Golovchenko, A.L. Simons, C.M. Surko, T.N.C. Venkatesan, *Appl. Phys. Lett.* **34**, 777–779 (1979)
16. M. Hauer, J.T. Dickinson, S.C. Langford, T. Lippert, A. Wokaun, *Appl. Surf. Sci.* **197**, 791–795 (2002)