Applied Surface Science 255 (2009) 5430–5434

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Shadowgraphy investigation of laser-induced forward transfer: Front side and back side ablation of the triazene polymer sacrificial layer

Romain Fardel [a,b,*], Matthias Nagel [a], Frank Nüesch [a], Thomas Lippert [b,**], Alexander Wokaun [b]

[a] Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Functional Polymers, Überlandstrasse 129, 8600 Dübendorf, Switzerland
[b] Paul Scherrer Institut, General Energy Research Department, 5232 Villigen PSI, Switzerland

ARTICLE INFO

Article history:
Available online 8 August 2008

Keywords:
Laser-induced forward transfer
Triazene polymer
Shadowgraphy imaging

ABSTRACT

Thin films of a photodecomposible triazene polymer are used as sacrificial layer for the micro-deposition of sensitive materials by laser-induced forward transfer. To understand the ablation process of this sacrificial layer, the ultraviolet laser ablation of triazene films was investigated by time-resolved shadowgraphy. Irradiation from the film side shows a complete decomposition into gaseous fragments, while ablation through the substrate causes ejection of a solid flyer of polymer. The occurence of the flyer depends on the film thickness as well as on the applied fluence, and a compact flyer is obtaind when these two parameters are optimized.

1. Introduction

Laser-induced forward transfer (LIFT) is a powerful and versatile method for the direct-write deposition of various materials. A transparent substrate (donor) is coated with a film of a material and placed close to a receiver substrate onto which the material shall be transferred. A laser pulse is imaged from the back side onto the donor film and induces a removal of the material at the irradiated spot with subsequent redeposition onto the receiver substrate [1–3]. Whereas the LIFT technique is readily applied to deposit metal films [4–6], sensitive materials cannot withstand direct irradiation and ablation. To overcome this limitation a sacrificial layer has been introduced between the donor substrate and the film to be transferred. This sacrificial layer is made of an aryltriazene polymer, which absorbs the laser light and protects the sensitive top layer from photodegradation and overheating. Upon irradiation, the triazene is decomposed into gaseous fragments, generating enough pressure to eject the top layer [7–10]. The modified LIFT technique has been succesfully applied to transfer organic light-emitting diode materials [11] as well as living cells [12], nanocrystal quantum dots [13] and metal [14].

Up to now, deposition was realised in close contact between the donor and receiver susbtrates but no satisfactory results were obtained if the substrates were separated by a gap. However, achieving transfer without having the substrates in contact would greatly facilitate alignment of the donor and receiver. For this reason, it is important to understand how the material is ablated and transferred when the substrates are separated by a gap. A suitable method for this study is lateral time-resolved shadowgraphy imaging [15], commonly used for imaging the ejection process in LIFT [16–18].

In this work, laser ablation and forward ejection of a single layer of an aryltriazene polymer was studied by time-resolved shadowgraphy. Front side and back side ablation were compared at different film thicknesses and fluences, and the occurence of a flyer was investigated.

2. Experimental

The triazene polymer (poly[oxy-1,4-phenylene(3-methyl-1-triazene-1,3-diyl)-1,6-hexanediyl(1-methyl-2-triazene-1,3-diyl)-1,4-phenylene]) was synthesized as described in [19] (compound TP-6a). Films were prepared on fused silica substrates by spin coating from polymer solutions in chlorobenzene and cyclohexanone (1:1, w/w).

The ablation experiments were performed with single pulses from a XeCl excimer laser (Compex, Lambda Physik, $\lambda = 308$ nm and $\tau = 30$ ns). A square mask with an aperture of 2 mm was used to select a homogeneous part of the beam, which was imaged by a lens onto the polymer film with a demagnification of 4, yielding a

* Corresponding author at: Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Functional Polymers, Überlandstrasse 129, 8600 Dübendorf, Switzerland. Tel.: +41 44 823 49 14; fax: +41 44 823 40 12.
** Corresponding author.
E-mail addresses: romain.fardel@empa.ch (R. Fardel), thomas.lippert@psi.ch (T. Lippert).

0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.07.187

spot size of 500 μm. The sample was placed on a motorized translation stage, with the film facing the laser beam for front side ablation and the opposite way for back side ablation. The fluence was controlled by an attenuator plate. The pulse energy was measured by a pyroelectric energy meter (Molectron J4-09 or Gentec QE 50) placed at the end of the beam line. Visualization of the process was achieved by a CMOS camera with a microscopic objective placed perpendicular to the laser beam, i.e., parallel to the sample surface, with the focus at the ablation spot. Back illumination was obtained by a probe laser (Nd:YAG, λ = 532 nm, τ = 6 ns) pumping a fluorescent dye (rhodamine), placed on the camera axis on the opposite sample side. The delay between the pump and probe laser pulses was set by a digital pulse/delay generator (Stanford Research Systems DG535). A computer controlled system allowed to vary the fluence, position and time delay, and to take a sequence of pictures. Each picture was recorded with a different pulse and corresponds to a new position on the sample. For estimating the thickness of the flyer, the triazene polymer was transferred onto glass substrates as described elsewhere [20]. The film thickness and ablation depth were measured by profilometry (Ambios XP1).

3. Results and discussion

3.1. Front side ablation

Ablation from the front side has been studied first, because most reference data exist for this configuration and therefore allow comparison with literature. It is also the most simple configuration, since the volume of ablated material is directly accessible from the crater depth measurement. A sequence of pictures taken at 110 mJ/cm^2 for a 500 nm thick triazene polymer film is shown in Fig. 1. The film surface is on the right, while the laser pulse comes from the left.

Two propagating features can clearly be distinguished in the images. The first moving front (feature A in Fig. 1) is attributed to the shock wave caused by the pressure jump at the ablation spot, where a large amount of gas is released during the laser pulse. The shock wave propagates first in a piston-like motion (at 0.2 μs), when the propagation distance is shorter than the width of the ablation spot. The shock front tends to become hemispherical when the distance increases, as expected for a point-like ablation spot [21].

The second observable feature (indicated as B in Fig. 1) is most probably formed by gaseous decomposition products from the polymer. The shape evolution of this product front is slightly different from the shock wave. Obviously expansion is slowing down very quickly and maintains a flat shape. The presence of the shock wave and the gas front corresponds to observations from previous work on thick films of a slightly different triazene polymer [22]. It is remarkable that no particles are visible in the ablation plume, which confirms a clean and debris-free ablation of the triazene observed previously [23,24].

The above described observations are also valid for a 190-nm thick sample (not shown). For thinner films, it was shown previously that the ablation threshold fluence strongly increases for thicknesses below 50 nm, due to heat diffusion and reduced absorption [23]. Therefore, a change in the behavior can be expected for films thinner than 50 nm.

3.2. Back side ablation

The corresponding configuration to analyse the LIFT process is the back side ablation. A sequence of pictures taken for a 460-nm thick triazene polymer film at a fluence of 110 mJ/cm^2 is presented in Fig. 2. The samples are rotated by 180° with respect to front side ablation (Fig. 1). The shock wave is also visible with a similar shape and expansion properties as observed for front side ablation. The main difference is the replacement of the product front seen in Fig. 1 with an opaque object ejected from the substrate, i.e., a flyer, which becomes visible 0.4 μs after the irradiation. The flyer has initially a well-defined flat shape, corresponding to the ablated spot of the polymer film. Then it expands, becomes distorted and looses its initial shape.

The angular distribution of the decomposition fragments of the flyer after longer distances were not investigated, because the goal

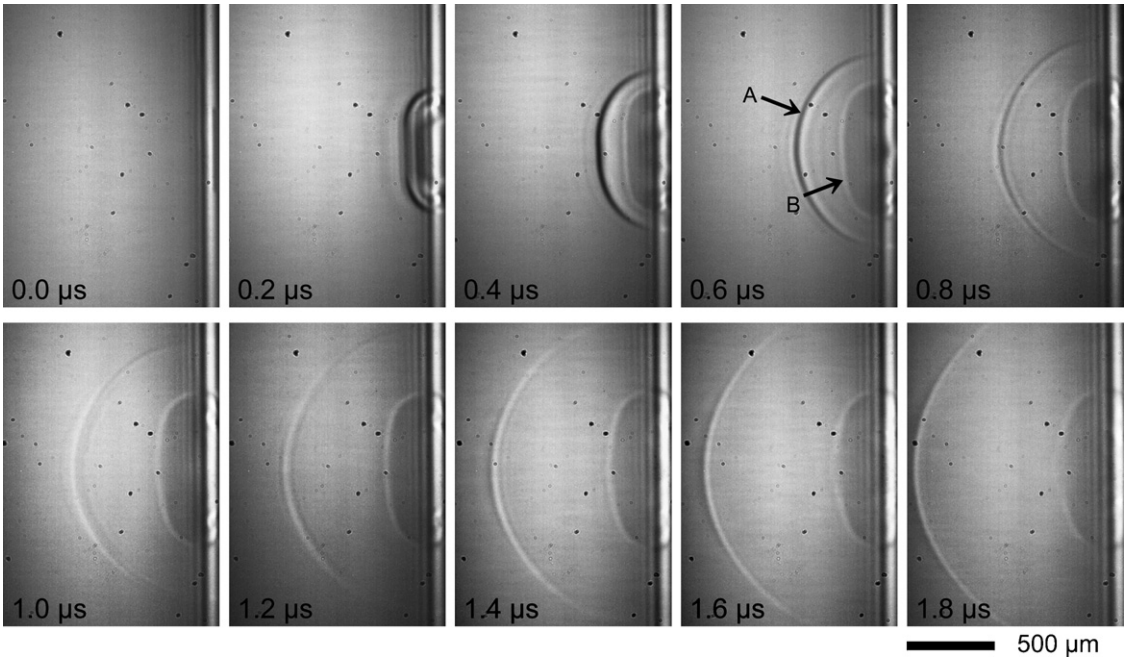

Fig. 1. Sequence of pictures taken for front side ablation of a 500 nm triazene polymer film at 110 mJ/cm^2. The laser comes in from the left, while the susbtrate is on the right. The time delays are indicated on the frames. The arrows show the features A and B described in Section 3.1.

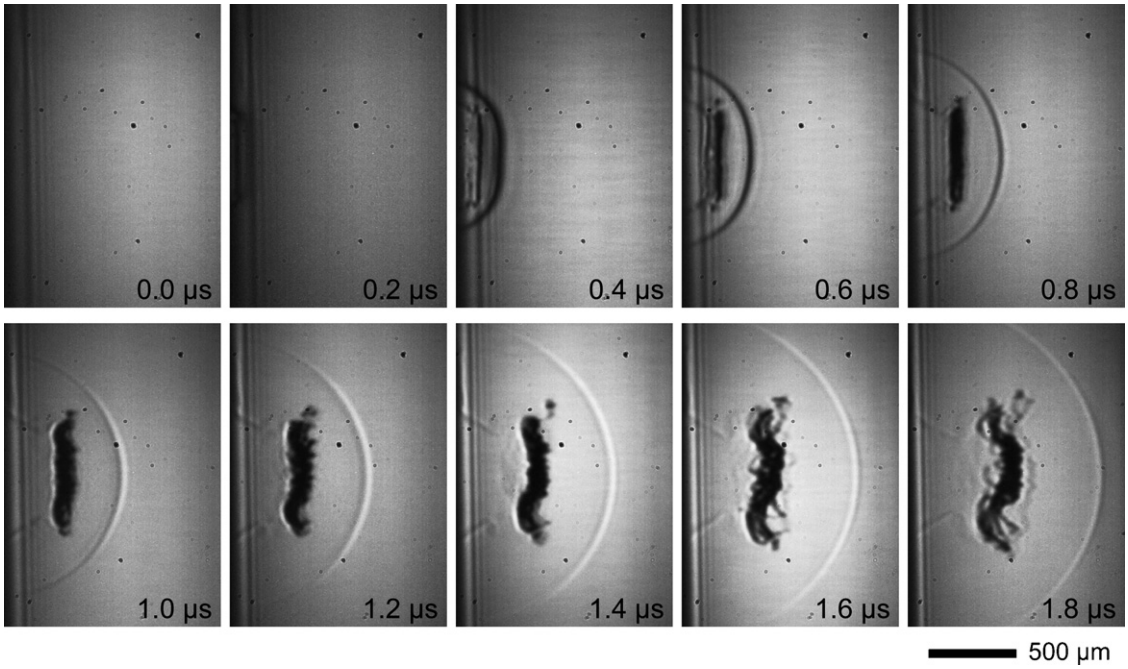

Fig. 2. Sequence of pictures taken for back side ablation of a 460 nm triazene polymer film at 110 mJ/cm^2. The time delays are indicated on the frames.

of the technique is to produce and transfer an intact flyer of material, and the data shown suggest that it happens only at a limited distance from the donor film.

The presence of the flyer shows that the entire triazene layer is not ablated by a single laser pulse at this fluence. The flyer consists of undecomposed polymer, which is ejected by the pressure thrust created during ablation and decomposition of the underlying part. This partial ablation upon back side exposure confirms previous observation in transfer experiments, where a triazene pellicle was still present on the ablated spot [20].

3.3. Effect of film thickness and fluence

The formation of a flyer requires that a certain amount of material stays intact, or at least, in the form of a compact product layer. The appearance, shape and properties of the flyer should depend on the irradiation fluence because the latter will determine the ablation depth, and therefore the thickness of the remaining polymer. The film thickness should also play a similar role, because for a given fluence, a thin film will be fully decomposed with no flyer present. To verify this assumption, samples with two film thicknesses (190 nm and 460 nm) were investigated for various fluences. A summary of these experiments is given in Fig. 3(a and b), where the time delay was kept constant at 1.2 µs. Corresponding optical microscopy pictures of the 460 nm thick sample after ablation are shown in Fig. 3(c).

In the case of the thicker film (Fig. 3b) at a fluence of 40 mJ/cm^2, which is close to the threshold fluence of 25 mJ/cm^2 [23], no flyer is observed and only the shock wave is visible. The corresponding microscopy picture shows the presence of a remaining skin layer at the ablated spot, which has probably been expanded and deflated after the pulse. In this case, no ejection of the top layer occurred, because the generated pressure was not sufficient to expel the top layer. A flyer can be observed when the fluence is increased. At 50 mJ/cm^2, the flyer remains very close to the substrate and seems not to be completely detached from the remaining polymer. The residues on the ablated spot confirm that a part of the flyer remains linked to the donor film, i.e., mainly at the corners [20], where polymer threads are visible. The flyer exhibits a good flat shape for an iradiation fluence of 70 mJ/cm^2, but the upper and lower parts seem to be still connected to the initial film. Above 110 mJ/cm^2, the flyer is clearly detached and no residues are present in the ablation spot. However, the shape of the flyer starts to be less well-defined and its size increases, together with its ejection speed. This can be assigned to the decreased thickness and therefore lower mechanical stability of the flyer. This fact is even more pronounced at 200 mJ/cm^2, where the flyer contour becomes more cloudy. Eventually, no flyer is visible and the whole layer of donor film is decomposed into gaseous products at a fluence $\geq$700 mJ/cm^2.

With increasing fluence, the penetration depth of the laser increases and a thicker layer of material is decomposed, generating more gaseous species, i.e., pressure to cause the ejection of the flyer. At the same time, the remaining film thickness decreases. With increasing fluence more energy is available to eject a flyer with a decreasing thickness which results in faster destabilization of the flyer. The final scenario is reached when the whole triazene thickness is ablated.

The effect of fluence on the thinner film (190 nm) is similar except that the flyer gets decomposed at lower fluences. Fig. 3(a) shows shadowgraphy pictures for the 190 nm thick triazene sample. At 40 mJ/cm^2, a partially detached cloudy piece is already visible, although no flyer is ejected. The best flyer, i.e., the flyer which has the best chance to yield a good deposition, is visible for a fluence of 50 mJ/cm^2. The flyer becomes less visible when the fluence is further increased and for 70 mJ/cm^2, it is not clear whether a solid flyer or only a cloud of gaseous species and fragments are ejected. Above this fluence, only gaseous ablation products are observed which have a similar appearance for a fluence of 200 mJ/cm^2 as the features observed for front side ablation.

For a given film thickness, the quality of the flyer changes constantly with an increase of the fluence. The best quality, i.e., flat shape and compact aspect, is reached for an intermediate fluence for both polymer thicknesses. However, this optimum fluence is

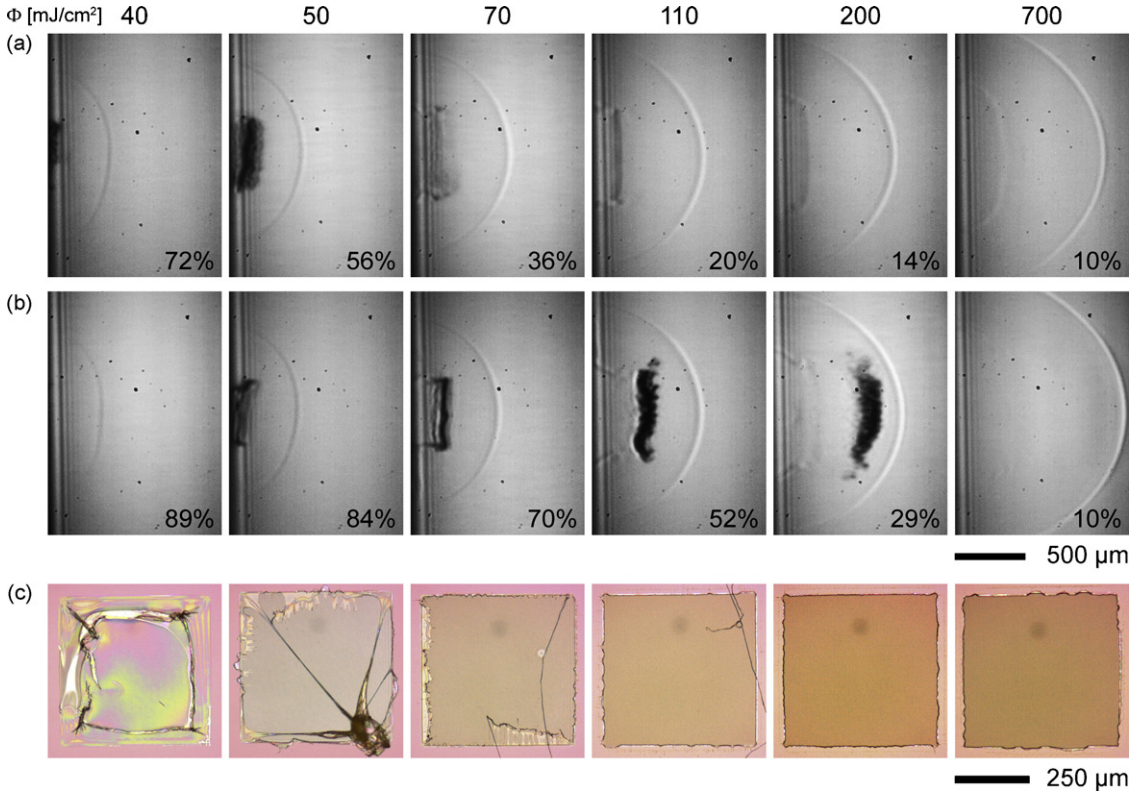

Fig. 3. Pictures of back side ablation taken after 1.2 ms with 190 nm (a) and 460 nm (b) triazene polymer films at increasing fluence (from left to right) and the corresponding ablation spot microscopy images of the 460 nm triazene sample ((c), at a different scale). The percent value on the pictures is the calculated undecomposed ratio (see Section 3.3 for details).

higher for the thicker sample (between 70 and 110 mJ/cm^2) than for the 190 nm film (around 50 mJ/cm^2). The thickness of the flyer was estimated in order to quantify this difference in optimum laser fluence. The ablation depth of the corresponding films was measured for front side ablation and is assumed to be the same for back side ablation. The flyer thickness should then be equal to the film thickness minus the ablated depth. This assumption is easy to calculate and should give a good approximation of the flyer thickness. The result is expressed in terms of percentage of the initial thickness and indicated in the corresponding pictures in Fig. 3. The optimum value to get a good yet well-separated flyer is between 60 and 80% of undecomposed layer. The sharpness of the flyer shape decreases strongly when this ratio is smaller than 50%. Eventually, the flyer is completely decomposed into fragments and gaseous species when the theoretical part of unaffected triazene thickness lies between 20 and 30%.

The percentage of undecomposed polymer seems to be a useful value for characterizing the process. A direct comparison of the images generated from the 460-nm and 190-nm thick films at the same fluence reveals that the flyer from the thinner film is faster and broader. Indeed, the ratio of undecomposed polymer is quite different for both samples. A direct comparison of the flyer properties should only be valid for fluences where a similar percentage of undecomposed thickness is obtained, i.e., 50 mJ/cm^2 for 190 nm and 110 mJ/cm^2 for 460 nm. In this case, both flyers have a comparable shape, but the flyer from the thicker sample is faster. This suggests that the calculated ratio is a good estimation of the flyer state and behavior, but additional effects are also important. The laser energy and the absolute amount of decomposed material play an important role in the process and a more comprehensive estimation of the energy balance is currently under investigation to understand the system in more details.

4. Conclusion

Time-resolved shadowgraphy imaging shows that front side ablation of the triazene polymer occurs in a clean way and produces no visible fragments. For back side irradiation, a flyer of polymer is observed under certain conditions. The shape and properties of the flyer depend substantially on the optimum relation between the film thickness and the laser fluence, which can be expressed as the precentage of undecomposed layer thickness. If this fraction is too high, only partial ejection is observed, while for lower percentages the flyer is fully decomposed. Correspondingly, formation of a compact flyer is restricted to a narrow parameter window.

Acknowledgement

Financial support from the Swiss National Science Foundation is gratefully acknowledged.

References

[1] J. Bohandy, B.F. Kim, F.J. Adrian, Journal of Applied Physics 60 (4) (1986) 1538–1539.
[2] K. Kyrkis, A. Andreadaki, D. Papazoglou, I. Zergioti, Direct transfer and microprinting of functional materials by laser-induced forward transfer, in: J. Perrière, E. Millon, E. Fogarassy (Eds.), Recent Advances in Laser Processing of Materials, vol. 241, Elsevier, Amsterdam, 2006, pp. 213–241..
[3] C. Arnold, P. Serra, A. Piqué, Mrs Bulletin 32 (2007) 23–31.
[4] I. Zergioti, S. Mailis, N. Vainos, C. Fotakis, S. Chen, C. Grigoropoulos, Applied Surface Science 127–129 (1998) 601–605.

[5] T. Sano, H. Yamada, T. Nakayama, I. Miyamoto, Applied Surface Science 186 (2002) 221–226.
[6] D.P. Banks, C. Grivas, J.D. Mills, R.W. Eason, I. Zergioti, Applied Physics Letters 89 (19) (2006) 193107–193113.
[7] D. Karnakis, T. Lippert, N. Ichinose, S. Kawanishi, H. Fukumura, Applied Surface Science 127–129 (1998) 781–786.
[8] T. Mito, T. Tsujita, H. Masuhara, N. Hayashi, K. Suzuki, Japanese Journal of Applied Physics, Part II. Letters 40 (8A) (2001) L805–L806.
[9] T. Lippert, J. Dickinson, Chemical Reviews 103 (2) (2003) 453–485.
[10] T. Lippert, Advances in Polymer Science 168 (2004) 51–246.
[11] R. Fardel, M. Nagel, F. Nüesch, T. Lippert, A. Wokaun, Applied Physics Letters 91 (2007) 061103.
[12] A. Doraiswamy, R. Narayan, T. Lippert, L. Urech, A. Wokaun, M. Nagel, B. Hopp, M. Dinescu, R. Modi, R. Auyeung, D. Chrisey, Applied Surface Science 252 (2006) 4743–4747.
[13] J. Xu, J. Liu, D. Cui, M. Gerhold, A.Y. Wang, M. Nagel, T.K. Lippert, Nanotechnology 18 (2) (2007) 025403.
[14] R. Fardel, M. Nagel, F. Nüesch, T. Lippert, A. Wokaun, Applied Surface Science 254 (2007) 1322–1326.
[15] S.F. Ray, High Speed Photography and Photonics, SPIE Press, Bellingham, 2002.
[16] B. Hopp, T. Smausz, N. Barna, C. Vass, Z. Antal, L. Kredics, D. Chrisey, Journal of Physics D: Applied Physics 38 (6) (2005) 833–837.
[17] D.D. Dlott, Applied Surface Science 197–198 (2002) 3–10.
[18] I. Zergioti, A. Karaiskou, D. Papazoglou, C. Fotakis, M. Kapsetaki, D. Kafetzopoulos, Applied Surface Science 247 (2005) 584–589.
[19] M. Nagel, R. Hany, T. Lippert, M. Molberg, F. Nüesch, D. Rentsch, Macromolecular Chemistry and Physics 208 (2007) 277–286.
[20] M. Nagel, R. Fardel, P. Feurer, M. Häberli, F. Nüesch, T. Lippert, A. Wokaun, Applied Physics A 92 (2008) 781–789.
[21] Y.B. Zel'dovich, Y.P. Raizer, Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena, Dover Publications, Mineola, NY, 2002.
[22] L. Bennett, T. Lippert, H. Furutani, H. Fukumura, H. Masuhara, Applied Physics A: Solids and Surfaces 63 (1996) 327–332.
[23] R. Fardel, M. Nagel, F. Nüesch, T. Lippert, A. Wokaun, B. Luk'yanchuk, Applied Physics A 90 (4) (2008) 661–667.
[24] R. Fardel, P. Feurer, T. Lippert, M. Nagel, F. Nüesch, A. Wokaun, Applied Surface Science 254 (2007) 1332–1337.