

Polymer Designed for Laser Applications-Fundamentals and Applications

Thomas Lippert^{*a}, Marc Hauer^a, Claude Phipps^b, Alexander Wokaun^a

^aPaul Scherrer Institut, 5232 Villigen PSI, Switzerland, ^bPhotonic Associates, 200A Ojo de la Vaca Road, Santa Fe, NM 87508, USA

ABSTRACT

The ablation characteristics of various polymers were studied at low and high fluences. The polymers can be divided into three groups, i.e. polymers containing triazene groups, designed ester groups, and reference polymers, such as polyimide. The polymers containing the photochemically most active group (triazene) exhibit the lowest threshold of ablation (as low as 25 mJ cm⁻²) and the highest etch rates (e.g. 250 nm/pulse at 100 mJ cm⁻²), followed by the designed polyesters and then polyimide. Neither the linear nor the effective absorption coefficients reveal a clear influence on the ablation characteristics. The different behavior of polyimide might be explained by a pronounced thermal part in the ablation mechanism. The laser-induced decomposition of the designed polymers was studied by nanosecond interferometry and shadowgraphy. The etching of the triazene polymer starts *and* ends with the laser pulse, clearly indicating photochemical etching. Shadowgraphy reveals mainly gaseous products and a pronounced shockwave in air. The designed polymers were tested for applications ranging from microoptical elements to polymer fuel for laser plasma thrusters.

Keywords: Laser ablation, photopolymers, triazene-polymer, shadowgraphy, interferometry, laser plasma thruster

1. INTRODUCTION

Laser ablation of polymers was first reported in 1982 and envisioned as a possible alternative or complementary technique to conventional photolithography.^{1,2} Laser ablation has the advantage of less processing steps, but up to now this potential could not be exploited with the commercially available polymers, such as polymethylmethacrylate (PMMA), polyimide (PI), and polycarbonate (PC) etc.³ These polymers reveal severe drawbacks, such as low sensitivity, carbonization upon irradiation, or ablation debris contaminating the surface and optics. Therefore novel photopolymers were developed to overcome these limitations.^{4,5,6,7}

Photochemical considerations have been applied for the design of these polymers. They were designed for an irradiation wavelength of 308 nm, because not all photolithographic processes require a resolution in the sub-micrometer range, and it is possible to de-couple the absorption of the photochemically active groups from the absorption of other parts of the polymer structure. This concept can be used to test whether the incorporation of photochemically active groups into the polymer chain improves the ablation characteristics. The XeCl excimer laser (308 nm) is a technically interesting tool, due to the long lifetime of gas fills and laser optics. The most promising approach for the design of these 'laser ablation polymers' is the incorporation of the photochemically active chromophore into the polymer main chain. In this way, the polymer is highly absorbing at the irradiation wavelength and decomposes exothermically at well-defined positions of the polymer back-bone into gaseous products.^{8,9} The gaseous products act as driving gas of ablation and carry away larger fragments, which could otherwise contaminate the surface. The polymers are therefore ablated without major modifications of the residual polymer surface, thus allowing a reproducible ablation.¹⁰

From the standpoint of ablation properties, triazene group (-N=N-N<) containing laser-resists (TP) have been identified as the most promising candidates. Unfortunately problems are encountered with the stability with respect to the following steps during a complete processing cycle, e.g. oxidation of the substrate.¹¹ Selected polyesters (PE) and polyester carbonates (PEC) have also been found to exhibit good ablation behavior.¹² The sensitivities of the PE's and PEC's are lower as compared to the triazene-based polymers, but they exhibit a higher chemical stability. These polymers also produce small gaseous products (CO₂, CO) upon decomposition.

*thomas.lippert@psi.ch; phone ++41-56-310-4076; fax ++41-56-310-2485; http://ecl.web.psi.ch/matdev/Laser_Proc/index.html

Novel polymers were synthesized to test whether it is possible to combine the sensitivity of the triazene polymers with the stability of the polyesters. These polyesters contain cinnamylidenemalonyl groups, and the triazene functional group. To compare the influence of these two chromophores (triazene vs. ester) polymers were synthesized containing the same ester group but with and without the triazene groups. The chemical structures of the polymers TM and MP are shown in Scheme 1. TM contains a triazene functional groups, whereas MP is the polyesters without the triazene groups. To compare the ablation properties of the new polymers several other polymers were included as references in this study, i.e. polyimide (PI, Kapton from Goodfellow) as representative of a highly absorbing 'standard' polymer, a commercial polyester (PE, Bayer AG) as representative of standard ester polymers, and TP, as representative of the original triazene polymer.

Previous studies had shown,¹¹ that laser ablation will not replace optical microlithography with photoresists, but may find applications in microstructuring and as a fast prototyping tool. Complex patterns, e.g. microoptical elements, can either be generated by scanning ablation tools, which are even capable of producing continuous topographies by varying the applied fluence on the material surface.¹³ Due to the sequential nature of the method, the throughput is very limited. A parallel patterning of larger areas requires a set-up comparable to photo steppers, where the mask structure is projected onto the substrate surface.¹⁴ One of the major problems of this method is the damage occurring in chromium absorber structures of standard photomasks at higher laser fluences.¹⁵ An alternative technique utilizes diffractive grating structures etched into a quartz mask blank to diffract the transmitted light out of the aperture of the projection optics¹⁶ (shown in Figure 1). This method combines the capability of scanning ablation tools to vary the ablated depth continuously with the high throughput of projection methods. An additional improvement can be achieved by the application of special photopolymers.

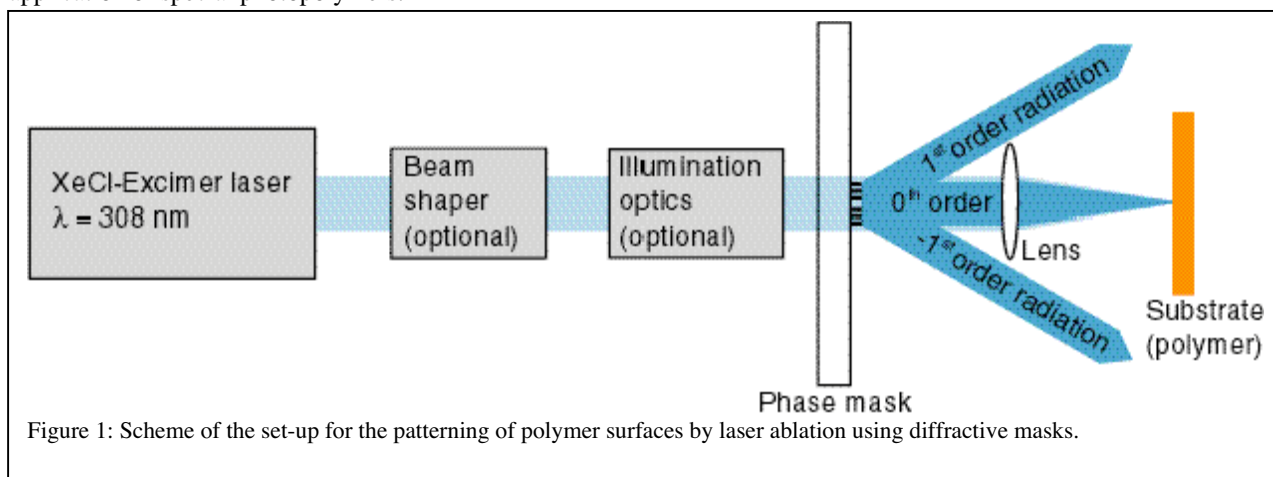


Figure 1: Scheme of the set-up for the patterning of polymer surfaces by laser ablation using diffractive masks.

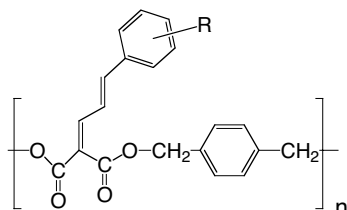
A very different application of laser ablation of polymers can be found in aerospace science. With the advent of microsattelites (>10kg), nanosatellites (1-10kg) and even picosatellites (< 1kg) it is necessary to develop steering engines which have a small mass (≤ 200 g) and size, produce a high specific impulse and are inexpensive. One promising candidate for this application are laser plasma thrusters (LPT's),^{17,18} which have some advantages over more common candidates for microthrusters, such as pulsed plasma thrusters or resistojets. The performance of the LPT's is to a large extent depending on the properties of the polymers used in these devices. The well-defined exothermic decomposition of the above mentioned photopolymers was an attractive feature to test these polymers also for an application with near-IR irradiation. Additional polymers, such as poly-vinylalcohol and other designed polymers, were also tested for this application (see scheme 1).

2. EXPERIMENTAL

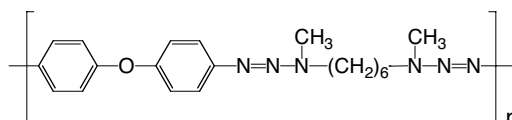
The synthesis of the triazene-polymer (structure shown in Scheme 1) was described in detail elsewhere.¹⁹ The polymers, TM and MP were synthesized using a standard polycondensation reaction. The synthesis is described in detail elsewhere.²⁰ The polyimide (Kapton) was obtained from Goodfellow, while Bayer AG supplied the polyester, and BASF the polyvinylalcohol. The linear absorption coefficients, α_{lin} , of the polymers used for ablation are compiled in Table 1.

A XeCl excimer laser (Lambda Physik, Compex 205; $\lambda = 308$ nm, $\tau = 20$ ns), was used as irradiation source for most experiments, with the exception of the interference experiments (see below) and the additional ablation studies at

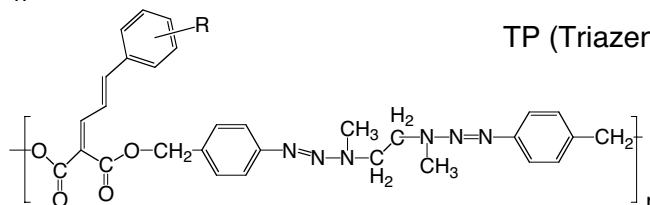
Designed Polymers



MP (Malonyl-Polyester)

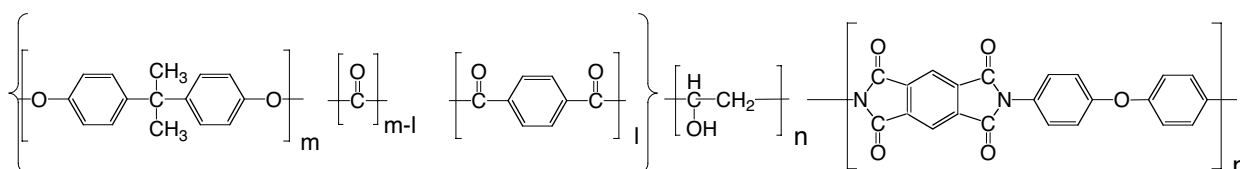


TP (Triazene-Polymer)



TM (Triazene-Malonyl-Polyester)

Reference Polymers



Polyester (PE, l=m)/Polyestercarbonate (PEC)

PVAIc

Polyimide (PI)

Scheme 1: Chemical structures of the designed and reference polymers.

different wavelengths. For these studies an ArF excimer laser (Lambda Physik, LPX300; $\lambda = 193$ nm, $\tau = 20$ ns) and a frequency quadrupled Nd:YAG (Quantel Brilliant B, $\lambda = 266$ nm) laser were applied. The polymer films (50 μm thick) for the laser ablation experiments were prepared by solvent casting with THF as solvent. To determine the etch rates of the polymers, a pinhole mask (diameter = 4 mm) was demagnified with a lens ($f = 100$ mm) onto the polymer surface to create circular craters. The pulse energy deposited on the sample was measured by a joulemeter (Gentec 200). The fluence for a constant spot size was varied between 10 mJ cm^{-2} and 10 J cm^{-2} using a dielectric attenuator (Laser Laboratorium Göttingen) and an additional beamsplitter (10% transmission) for the low fluences. The number of pulses delivered to the sample was controlled by a pneumatic shutter. For a typical experiment, a 10 x 10 matrix of circular craters was created on every polymer film, while varying the fluence and the pulse number. All ablation experiments were performed in air. The depth of the ablated craters was measured with the surface profiler. The ablation experiments were performed at low (10 - 400 mJ cm^{-2}) and high fluences (0.5 - 10 J cm^{-2}) to investigate the ablation behavior of the polymers over a broad fluence range.

The experimental set-up for the time-resolved (ns) surface interference fringes and shadowgraphy has been described in detail elsewhere.²¹ We use a modified version of this setup, described in detail elsewhere.²²

The polymer films were prepared by spin coating (1-5 μm thick) onto quartz wafers, e.g. for the fabrication of microoptical elements or by solvent casting (up to 250 μm). The polyimide (125 μm thick sheets of Kapton[®] from Goodfellow) was used as received. The phase masks were prepared by electron beam lithography, as reported elsewhere.²³

For the IR irradiation experiments (LPT application) carbon-doped polymer films (designed polymers and polyvinylalcohol, PVAIc, as reference polymer) were prepared onto polymer substrates (PET or PI or Acetate). The performance of the films was determined by irradiation with a diode laser (SDL, Inc. XC30) and a special developed torsion balance (sensitivity as low as 10^{-10} N s), described in detail elsewhere.¹⁸

3. RESULTS AND DISCUSSION

3.1. Ablation characteristics

All polymers in this study can be classified as highly absorbing polymers ($\alpha_{\text{lin}} \geq 8000 \text{ cm}^{-1}$ at the irradiation wavelength of 308 nm), as shown in Table 1. The absorbance of the designed polymers (MP and TM) can be tuned by varying the substituent R. We selected R to obtain a similar α_{lin} (and different) which would allow a direct comparison of the polymers. This could be accomplished for the high end of absorptivity for four different polymers, i.e. TP, TM, MP, and PI. The polymers were studied at low fluences which offer the opportunity to study the influence of structural parameters on the ablation rates. The high fluence range is mainly interesting for applications where high ablation rates in small areas are important, e.g. drilling or cutting. The ablation rates are mainly governed by processes in the created plasma, such as inverse Bremsstrahlung, but etch rates of up to 3 $\mu\text{m}/\text{pulse}$ could be achieved for TP. The low fluence range is also important for lithographic applications, where the cost of the photons is important. Low fluences may be defined from 10 to 400 mJ cm^{-2} . The ablation rates of the designed polymers (MP's, TM's and TP) can be divided into two groups with respect to the etch rates. All triazene-containing polymers have significantly higher ablation rates than the other polymers. The designed polyesters (MP's), as well as PE, reveal a higher etch rate than PI. The ablation rate is independent from α_{lin} (see Table 1 and Figure 2) and determined by the chemical structure. The ablation rates of non-triazene containing polymers, MP's, are approximately 100 nm/pulse , which is about half the value of the triazene containing polymers, TM's and TP. A slightly higher ablation rate is obtained for TP, which has the highest triazene density per polymer chain. The etch rates of the polyester (PE) and polyimide are about 60 nm/pulse which is again about half of the value of the designed polyesters. This is remarkable because the linear absorption coefficients of the designed polyesters cover the same broad range as PE and PI.

The ablation parameters, α_{eff} (effective absorption coefficient) and F_{th} (threshold fluence) were calculated according to the Equation (1),^{24,25}

$$d(F) = \frac{1}{\alpha_{\text{eff}}} \ln\left(\frac{F}{F_{\text{th}}}\right) \quad (1)$$

where $d(F)$ is the ablation rate (ablation depth per pulse) and are summarized in Table 1.

Table 1: Chemical properties and ablation parameters of the polymers.

	α_{308} ^{a)} (cm^{-1})	ϵ_{308} ^{b)} ($\text{M}^{-1} \text{cm}^{-1}$)	$\alpha_{\text{eff}} \text{LF}^{\text{c)}$ (cm^{-1})	$F_{\text{th}} \text{LF}^{\text{e)}$ (mJ cm^{-2})
MP1 (R=H)	102000	27400	50700 ± 2100	63 ± 3
MP2 (R=OCH ₃)	32000	7100	57000 ± 2000	48 ± 3
TM1 (R=H)	69000	57000	56100 ± 3400	27 ± 2
TP	100000	27700	49800 ± 2900	27 ± 2
TM2 (R=OCH ₃)	92000	35600	53300 ± 2500	28 ± 2
PI	95000	n.m.	83300 ± 3400	60 ± 3
PE	8000	1000	51500 ± 3200	73 ± 4

^{a)} linear absorption coefficient at 308 nm determined by UV-spectroscopy and profilometry.

^{b)} Molar extinction coefficient measured in solution.

^{d)} effective absorption coefficient calculated from equation 1 at low fluences (LF).

^{e)} threshold fluence calculated from equation 1 at low fluences.

^{f)} effective absorption coefficient calculated from equation 1 at high fluences.

^{g)} threshold fluence calculated from equation 1 at high fluences.

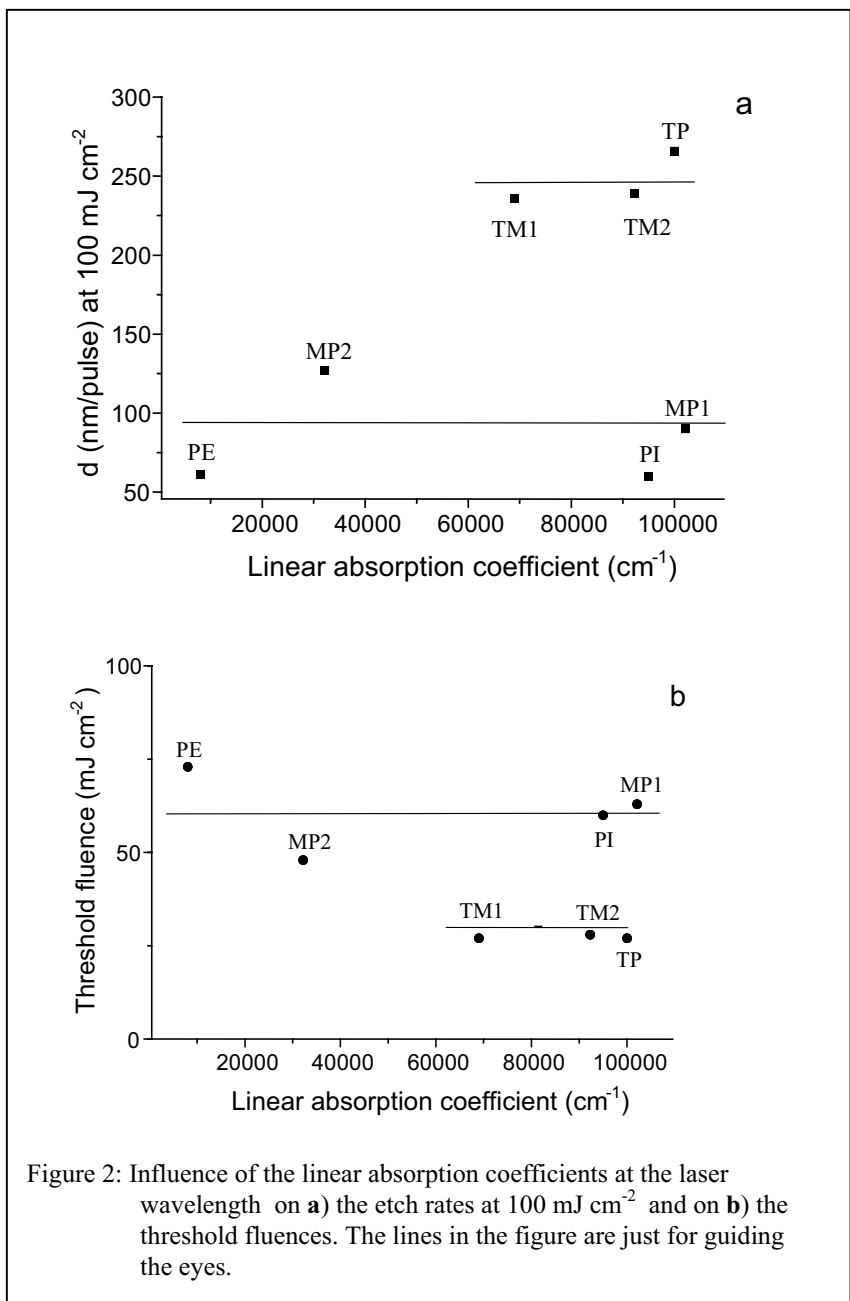
n.m.: not measured (insoluble).

The effective absorption coefficients, α_{eff} , calculated at low fluences, are much larger than the values obtained at high fluences. The effective absorption coefficients do not correlate with the linear absorption coefficients (Table 1),

may be with the exception of PI. A difference between the values of α_{eff} and α_{in} is observed for most polymers. An important feature is the similarity of α_{eff} for all designed polymers, including PE ($\approx 54000 \pm 5000 \text{ cm}^{-1}$), while PI reveals a much higher value (Table 1).

From an economic point of view, a polymer with a threshold fluence as low as possible is most desirable. The threshold fluences of the triazene containing polymers, TM's and TP, are about 30 mJ/cm^2 , which is much lower than those for the non-triazene containing polymers, MP's ($\approx 60 \text{ mJ cm}^{-2}$). These values are, to our knowledge, the lowest threshold fluence reported for laser ablation of polymers at 308 nm. The threshold fluence of TP obtained from this study is in good agreement with the value determined previously by UV-spectroscopy.²⁶ The calculated threshold fluences (from Equation 1, shown in Table 1) agree also very well with the experimentally observed threshold²⁷

fluences. A comparison of all polymers is shown in Figure 2. The linear absorption coefficients of the polymers are plotted against the etch rate at a fluence of 100 mJ cm^{-2} (Fig. 2a) and against the threshold fluence (Fig. 2b). Among the triazene containing polymers TP reveals the highest activity, probably due to the highest density of triazene groups in the polymer chain, resulting in larger amounts of nitrogen as product. The same order of activity is also confirmed by other experimental techniques, i.e. irradiation of the polymer in solution and mass spectrometry. The triazene containing polymers decompose much faster during irradiation in solution,²⁸ where thermal effects should be of only minor importance. In the mass spectroscopy studies a much higher amount of gaseous products is detected for the triazene containing polymers, confirming of course the higher etch rates, but also the role and importance of the gaseous species. These very pronounced differences are even more remarkably if we consider that the polymers were selected for similar absorption properties. At least one polymer out of each group has a comparable, linear absorption coefficient ($97000 \pm 5000 \text{ cm}^{-1}$), i.e. TP and TM for the triazene containing polymers, MP for the designed polyesters and PI for the reference polymers (see Fig. 2). This ensures that a direct comparison of these polymers is possible, due to the deposition of the laser energy within the same volume of the polymer. If the effective absorption coefficient is considered, then the triazene polymers can still be compared to the polyesters because their values



are again quite similar ($54000 \pm 5000 \text{ cm}^{-1}$). Only PI reveals a quite different effective absorption coefficient, similar to

the value of the linear absorption coefficient. Whereas the effective absorption coefficients are comparable, very pronounced differences between the triazene containing polymers and the polyesters are obtained for the ablation activity. This suggests that α_{eff} is of only minor importance for the ablation performance. The same is true for the linear absorption coefficients, because a variation of α_{lin} within one group of polymers has again no pronounced influence as seen when comparing, e.g. MP's (see Fig. 2). It is probably more important for its value to lie above a certain threshold (approx. 10000 cm^{-1}), where direct ablation without incubation is observed.

3.2. Time-resolved Measurements

Various time-resolved measurements were performed to probe the ablation mechanisms for selected polymers, e.g. TP. Time resolved transmission studies have shown that bleaching of the triazene chromophore takes place during the laser pulse.²⁶ Nanosecond shadowgraphy reveals that only gaseous products are formed and that the decomposition enthalpy of the polymer supports the resulting shock wave in air. The speed of the shock wave is fastest for the designed polymers and energetic polymers, probably due to the higher amount of gaseous products.²² Nanosecond interferometry reveals that etching of TP starts and ends with the laser pulse (details are reported elsewhere²²). A different behavior, i.e. pronounced swelling and delayed etching is detected for PI, which has been interpreted previously as indication for a thermal ablation mechanism. We also performed time-of-flight mass spectrometry (TOF-MS) measurements for the TP polymer at two irradiation wavelengths (248 and 308 nm). N_2 was identified as main decomposition product. A detailed analysis of the TOF curves shows that there exist 3 different species of N_2 originating from TP.

A metastable (excited) N_2 , with kinetic energies between 1 and 2 eV.

A very fast ground state N_2 , with kinetic energies of up to 6 eV.

A slow N_2 , with a very broad kinetic energy distribution that can be described by a decaying Maxwell-Boltzmann function.

The metastable and fast ground state N_2 species are hard to explain by a thermal mechanism. Details of these measurements are described elsewhere.^{9,29}

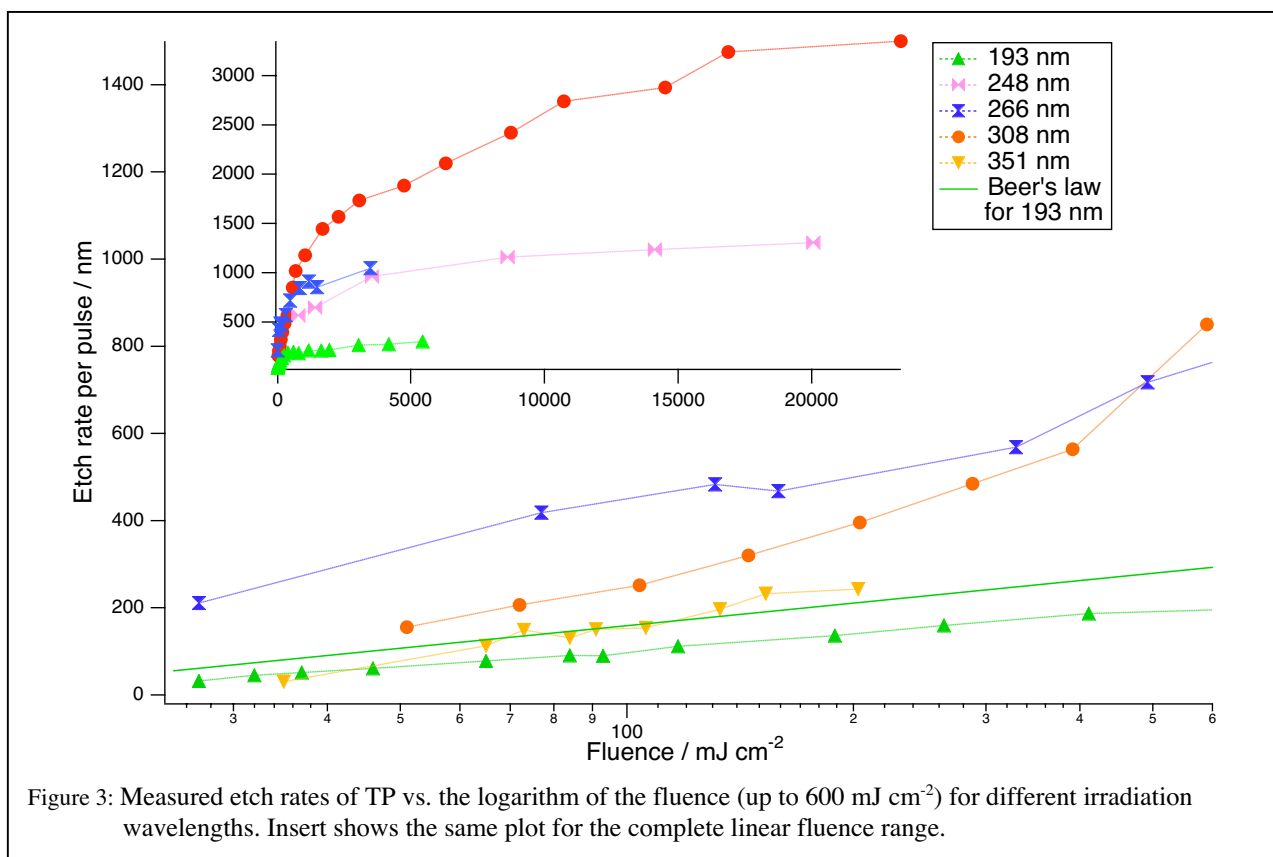


Figure 3: Measured etch rates of TP vs. the logarithm of the fluence (up to 600 mJ cm^{-2}) for different irradiation wavelengths. Insert shows the same plot for the complete linear fluence range.

3.3. Irradiation of TP at other wavelengths

Another important aspect of ablation is the dependence of ablation parameters on the irradiation wavelength. The correlation between absorption bands, irradiation wavelengths, and ablation behaviour was studied with various irradiation wavelengths, i.e. 193, 266, 308 and 351 nm. In Figure 3 the etch rates observed with TP for the different irradiation wavelengths are shown for low fluences on a logarithmic scale and on a linear scale for the complete fluence range (insert in Figure 3). In the high fluence range data points for 248 nm irradiation from a previous study⁴ are included. The data points seem to fit quite well to the 266 nm irradiation data. The different irradiation wavelengths correspond to different features of the UV-Vis spectrum. The spectrum reveals two strong bands around 196 nm, corresponding mainly to the aromatic parts of the polymer, and 332 nm, corresponding mainly to the triazene chromophore.²⁶ The etch rates can more or less be divided into two groups, i.e. the wavelengths which directly excite the triazene system (266, 308 and may be 351 nm) and 193 nm that is in resonance with the aromatic system. Irradiation with 193 nm results in the lowest ablation rates, which are even below the etch rates described by Equation 1 using the linear absorption coefficient α_{lin} from Beer's law (included in Figure 3). This is very different to the other irradiation wavelengths, where much higher etch rates result than predicted by Beer's law. This is most probably due to decomposition (ablation, see above) of the polymer during the pulse. The difference between 308 and 193 nm is even more remarkable when we consider that the absorption coefficients are quite similar. The etch rates of the three wavelengths which are in resonance with the triazene chromophore follow, at low fluences, the values of photon energy (highest photon energy = highest etch rate). The initial decomposition step is the triazene system, where homolytic bond breakage of the N-N single bond can be achieved with the energy of a single photon at all irradiation wavelength.

3.4. Applications

3.4.1. Microoptical elements: UV-irradiation

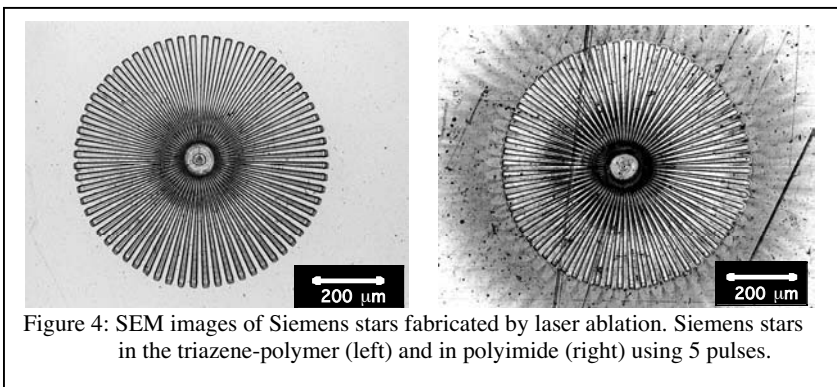


Figure 4: SEM images of Siemens stars fabricated by laser ablation. Siemens stars in the triazene-polymer (left) and in polyimide (right) using 5 pulses.

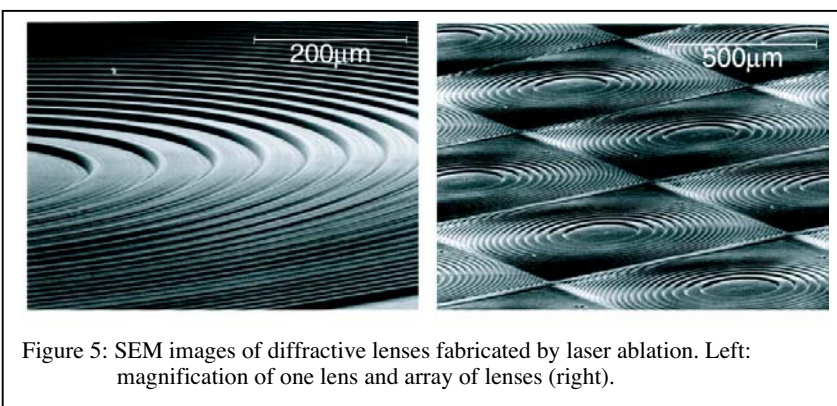


Figure 5: SEM images of diffractive lenses fabricated by laser ablation. Left: magnification of one lens and array of lenses (right).

The phase masks were designed for 308 nm as irradiation wavelength to demonstrate the potential of laser ablation as microfabrication technique. The ablation depths were measured after ablation using phase masks with various duty cycles. The ablation depths follow the scalar diffraction theory quite well. Deviations can be explained by the non-linear ablation behavior and the existence of a fluence threshold for ablation. Including these parameters into the design of the phase masks improves the efficiency of the ablated structures, e.g. gratings, by a factor of 2.¹⁶

Various structures were ablated into the special designed triazene-polymers and polyimide. It has been shown, that the decomposition products of the triazene polymer are mainly gaseous,⁸ which do not contaminate the surface, and that ablation occurs without modification of the remaining polymer surface.¹⁰ In the case of polyimide and most

commercial polymers, solid ablation products and carbonization of the polymer surface has been detected.³⁰ Examples of Siemens stars etched in TP and and PI are shown in Figure 4. The modified and re-deposited material is clearly visible around the ablated structure of the polyimide (right), but is absent for the triazene-polymer (left). Any surface

contamination or modification will deteriorate the performance of the microoptical elements and render the ablation rates unpredictable. The superior material, i.e. TP, was used to create a Fresnel lens and lens array (Figure 5). The ablation structures are well defined and can be created fast and easy. The higher sensitivity and etch rates of the triazene-polymer allows the application of larger phase masks. Alternatively, less pulses are necessary to fabricate an optical element with a given depths of the structures.

3.4 Laser Plasma Thruster: Near-IR irradiation

To analyze the performance of the polymer films for LPT's the target momentum was measured by the torsion balance and used to calculate the momentum coupling coefficient, C_m . This quantity is defined as

$$C_m = \frac{m\Delta v}{W}$$

with $m\Delta v$ as the target momentum produced during the ejection of laser-ablated material. W is the incident laser pulse energy. Another important parameter for thrusters is the specific impulse I_{sp} , which is defined as

$$C_m Q^* = v_E = I_{sp} g$$

Q^* is the specific ablation energy (incident power/mass ablation rate), v_E is the exhaust velocity and g is the acceleration due to gravity.

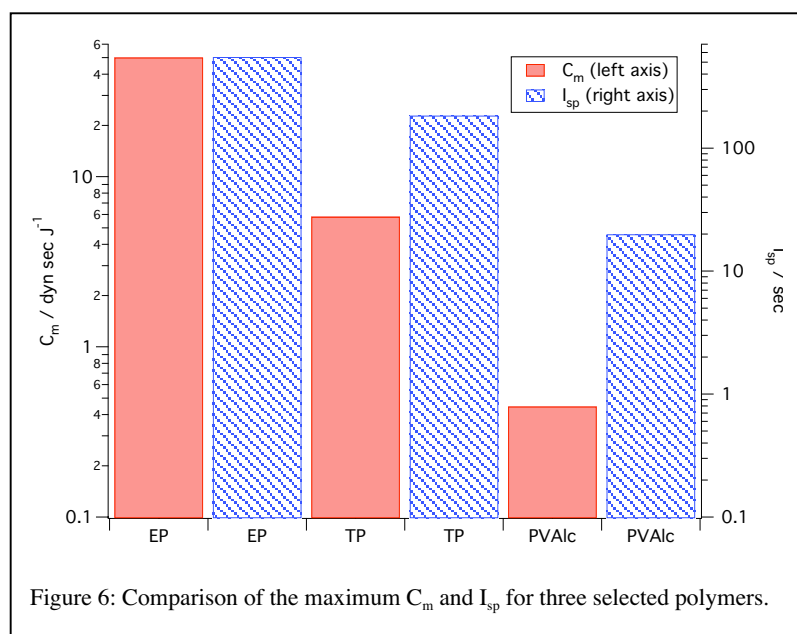


Figure 6: Comparison of the maximum C_m and I_{sp} for three selected polymers.

The measurements were performed in the transmission mode, which is the most probable candidate for LPT's. PET, PI or Acetate were chosen as substrates with a thickness of $\geq 75 \mu\text{m}$. Three polymers were selected for the tests, i.e. a polymer designed for laser ablation (triazene-polymer) in the UV, an energetic polymer (EP), and a commercial polymer (polyvinylalcohol, PVAIc). All polymers pass the fundamental requirements for LPT's. The polymers give homogenous films with a good adhesion on the substrates; they do not stick to each other; they are elastic over a broad temperature range (-50 to + 60 °C) and have an optical density (OD) of about 1. The latter requires that it is possible to dope the films homogenous with carbon. Most polymers have to be doped to accomplish an effective absorption in the near-IR. Carbon was chosen as dopant due

to the broad homogenous absorption over the whole near-IR range. The films of both polymers were prepared with an optical density of ≈ 0.9 and a thickness of 60 to 260 μm .

In Figure 6 the maximum values of the momentum coupling coefficients (C_m) and specific impulse (I_{sp}) are compared on a logarithmic scale. The PVAIc reveals the lowest values for C_m and I_{sp} , followed by TP and the energetic polymer. The values for the EP are among the highest obtained values for a non-confined material.³¹ Improvements of one order of magnitude are obtained for C_m from PVAIc to TP and EP.

4. CONCLUSIONS

The ablation characteristics of various polymers were studied. The polymers can be divided into three groups, polymers containing triazene groups, designed polyesters, and polyimide as reference polymer. The polymers containing the photochemically most active group (triazene) are also the polymers with the lowest threshold of ablation and the highest etch rates, followed by the designed polyesters and then polyimide. No pronounced influences of the absorption coefficients, neither α_{in} nor α_{eff} , on the ablation characteristics are detected. The clear difference between PI and the designed polymers might be explained by a pronounced thermal part in the ablation mechanism of PI, while

photochemical activities are more important for the triazene-polymer. The time-resolved measurements also support a pronounced photochemical part in the ablation mechanism.

The combination of phase masks and specially designed, highly sensitive photopolymers can be used for an efficient fabrication of 3-dimensional topographies using laser ablation. The application of the triazene-polymer, which has a very low threshold fluence, a high ablation rate and decomposes without contamination of the surface, allows a fast fabrication of microoptical elements. Designed polymers reveal also superior properties for LPT applications, where IR wavelengths are used. The energetic polymer revealed exceptionally high momentum coupling coefficients, followed by the designed photopolymer and a commercial polymer.

5. ACKNOWLEDGEMENTS

This work has been supported by the Swiss National Science Foundation and by the U.S. Air Force Office of Scientific Research. Nitrochemie Wimmis, BASF and BAYER have made some materials available.

6. REFERENCES

- ¹ R. Srinivasan, V. Mayne-Banton, *Appl. Phys. Lett.* **41**, 576, 1982.
- ² Y. Kawamura, K. Toyoda, S. Namba, *Appl. Phys. Lett.* **40**, 374, 1982.
- ³ K. Suzuki, M. Matsuda, T. Ogino, N. Hayashi, T. Terabayashi, K. Amemiya, *Proc. SPIE* **2992**, 98, 1997.
- ⁴ T. Lippert, J. Stebani, J. Ihlemann, O. Nuyken, A. Wokaun, *Angew. Makromol. Chem.* **206**, 97, 1993.
- ⁵ T. Lippert, J. Stebani, J. Ihlemann, O. Nuyken, A. Wokaun, *J. Phys. Chem.* **97**, 12296, 1993.
- ⁶ T. Lippert, T. Kunz, C. Hahn, A. Wokaun, *Recent Res. Devel. in Macromol. Res.* **2**, 121, 1997.
- ⁷ O. Nuyken, U. Dahn, N. Hoogen, D. Marquis, M. N. Nobis, C. Scherer, J. Stebani, A. Wokaun, C. Hahn, T. Kunz, T. Lippert, *Polym. News* **24**, 257, 1999.
- ⁸ L. S. Bennett, T. Lippert, H. Furutani, H. Fukumura, H. Masuhara, *Appl. Phys. A* **63**, 327, 1996.
- ⁹ T. Lippert, S. C. Langford, A. Wokaun, S. Georgiou, J. T. Dickinson, *J. Appl. Phys.* **86**, 7116, 1999.
- ¹⁰ T. Lippert, T. Nakamura, H. Niino, A. Yabe, *Macromolecules* **29**, 6301, 1996.
- ¹¹ T. Lippert, J. Wei, A. Wokaun, N. Hoogen, O. Nuyken, *Appl. Surf. Sci.* **168**, 270, 2000.
- ¹² T. Kunz, J. Stebani, J. Ihlemann, A. Wokaun, *Appl. Phys. A* **67**, 347, 1998.
- ¹³ N. H. Rizvi, P. T. Rumsby, M. C. Gower, *Proc. SPIE* **3898**, 240, 1999.
- ¹⁴ E. C. Harvey, P. T. Rumsby, *Proc. SPIE* **46**, 26, 1998.
- ¹⁵ J. T. Yeh, *Proc. SPIE* **922**, 461, 1988.
- ¹⁶ C. David, J. Wei, T. Lippert, A. Wokaun, *Microelectr. Eng.* **57-58**, 453, 2001.
- ¹⁷ C. R. Phipps, J. Luke, *Proc. SPIE* **4065**, 801, 2000.
- ¹⁸ C. R. Phipps, J. Luke, *AIAA Journal* **40**, 310, 2002.
- ¹⁹ J. Stebani, O. Nuyken, T. Lippert, A. Wokaun, *Makromol Chem. Rapid Commun.* **14**, 365, 1993.
- ²⁰ N. Hoogen, O. Nuyken, *J. Polym. Sci. Polym. Chem.* **38**, 1903, 2000.
- ²¹ H. Furutani, H. Fukumura and H. Masuhara, *Appl. Phys. Lett.* **65**, 3413, 1994.
- ²² T. Lippert, M. Hauer, D. J. Funk, A. Wokaun, paper 4760-33, this conference.
- ²³ C. David, D. Hambach, *Microelect. Engineering* **46**, 219, 1998.
- ²⁴ J. E. Andrews, P. E. Dyer, D. Forster, P. H. Key, *Appl. Phys. Lett.* **43**, 717, 1983.
- ²⁵ R. Srinivasan, B. Braren, *J. Polym. Sci.* **22**, 2601, 1984.
- ²⁶ T. Lippert, L. S. Bennett, T. Nakamura, H. Niino, A. Ouchi and A. Yabe, *Appl. Phys. A* **63**, 257, 1996.
- ²⁷ Defined as the fluence range where the onset of ablation could be measured with the profilometer.
- ²⁸ J. Wei, N. Hoogen, T. Lippert, O. Nuyken, A. Wokaun, *J. Phys. Chem. B* **105**, 1267, 2001.
- ²⁹ T. Dickinson, M. Hauer, T. Lippert, A. Wokaun, S. C. Langford, paper 4760-32, this conference.
- ³⁰ F. Raimondi, S. Abolhassani, R. Brüttsch, F. Geiger, T. Lippert, J. Wambach, J. Wei, A. Wokaun, *J. Appl. Phys.* **88**, 1, 2000.
- ³¹ C. R. Phipps, J. Luke, G. McDuff, T. Lippert, paper 4760-104, this conference.