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Polymers for UV and near-IR irradiation

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Abstract

Photopolymers designed for UV laser ablation were tested in quite different applications at very different irradiation wavelengths, i.e. in the UV (308 nm) and in the near-IR (935 nm). Diffractive gray tone phase masks were optimized for laser ablation and used to fabricate micro-optical elements. The application of the photopolymers (triazene-polymers) allowed a faster processing due to the high sensitivity, and showed less contamination of the surface by ablation products. The designed polymers also revealed superior properties for applications in the near-IR. Near-IR irradiation is used to create a plasma which could be used as a thruster for microsatellites. The carbon-doped triazene-polymer shows higher values of the momentum coupling coefficient and specific impulse than a commercial polymer. The well-defined threshold for the momentum coupling coefficient was only observed for the designed polymer. This threshold is an important feature for the design of real laser plasma thrusters for microsatellites. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photopolymer; Ablation; Micro-optics; Phase mask; Laser plasma thruster

1. Introduction

During the last decade, processing of polymers has become an important field of applied and fundamental research. One of the newer exciting fields of polymer processing is the application of lasers, ranging from the UV to the IR. Major concerns for industrial applications, especially of UV-lasers, are the high cost of photons and the efficient utilization of the photons, i.e. the sensitivity of the polymers to laser irradiation [1]. Other concerns are the resolution of laser processing and contamination of the surface and optics by the ablation products. Complex patterns, e.g. micro-optical 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 [2]. 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 [3]. One of the major problems of this method is the damage occurring in chromium absorber structures of standard photo masks at higher laser fluences [4]. 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 optics [5] (shown in Fig. 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. These polymers are highly sensitive to laser radiation, and decompose exothermically into gaseous products without contamination of the remaining polymer surfaces [6–8]. The threshold of ablation and etch rate of these polymers are at least a factor 2–3 lower and higher, respectively, than of standard polymers [9,10]. The polymers were designed for an irradiation wavelength of 308 nm. This wavelength has the advantage of the long lifetime of the laser optics and laser gas fills. The possible resolution of $\leq 1\ \mu m$ with our set-up is also sufficient for many applications.

A very different application of laser ablation of polymers can be found in aerospace science. With the advent of microsatellites (>10 kg), nanosatellites (1–10 kg) and even picosatellites (<1 kg), 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 (LPTs) [11,12], which have some advantages over more common candidates for microthrusters, such as pulsed plasma thrusters or resistojets. One quite serious problem with existing nozzle thrusters is that unpredictable physical regimes are entered when the dimension of the nozzles are

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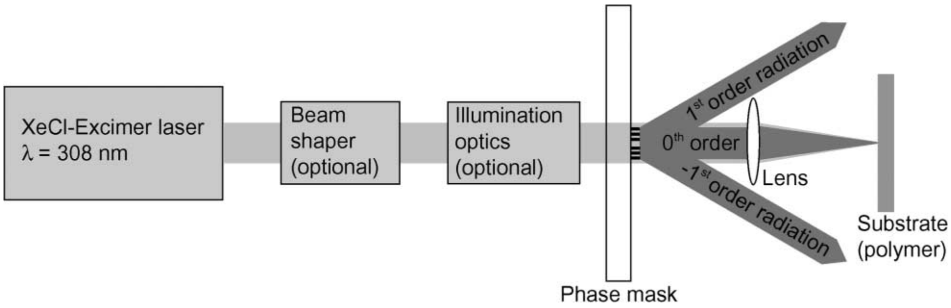


Fig. 1. Scheme of the set-up for the patterning of polymer surfaces by laser ablation using diffractive masks.

so small that the gas flow can no longer be described by the theory of viscous flow, which is the case for a 1 μm nozzle at a pressure of 10 bar. Nozzles are not necessary for LPTs, because the plasma expansion is already similar to a nozzle expansion. Another advantage of a LPT is the possible higher maximum specific impulse and the high efficiency of ≈50%. For chemical rockets the maximum impulse is about 500 s, limited by the available temperatures, while a specific impulse of 8000 s was reported for laser ablation of Al [13]. Due to the specific demands, i.e. weight and power, of small satellites, small powerful ($\geq$1 W) diode laser must be used. These lasers emit in the near-IR (930–980 nm) with an available power of around 1–5 W and pulse lengths from 100 μs to the ms range. Fluences of several hundred joules per centimeter square can be achieved with standard optical components (laser spot diameter around 5 μm). The long pulse lengths of the diode lasers restrict the applicable materials to polymers, which have low thermal conductivities. It was for example not possible to create a plasma with the previously mentioned diode lasers on Al. The performance of the LPTs 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.

2. Experimental

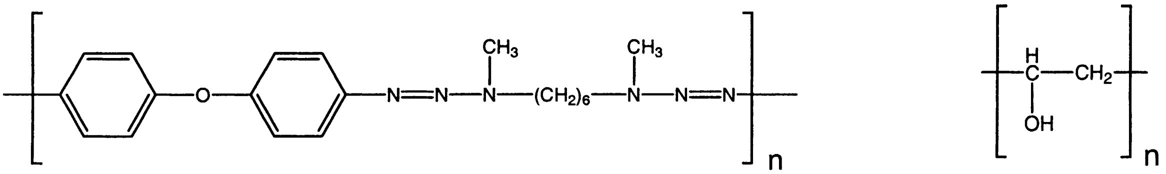
The synthesis of the triazene-polymer (structure shown in Scheme 1) was described in detail elsewhere [14]. Thin films (1–5 μm thick) of the triazene-polymer were spin-coated onto quartz wafers for the fabrication of micro-optical elements. As spincoating solution, 15 wt.% of the polymer in chlorobenzene was used. The polyimide (125 μm thick sheets of Kapton® from Goodfellow) was used as received. A XeCl excimer laser (Lambda Physik, Compex 205) was used as irradiation source. The phase masks were prepared by electron beam lithography, as reported elsewhere [15].

For the carbon-doped triazene-polymer films chlorobenzene was used as solvent, while for the carbon-doped polyvinylalcohol (PVAlc, Alcotex™, Hoechst) a water/methanol mixture was used. The polymer solutions were combined with carbon (0.5 wt.%, Ketjen Black, BASF) suspensions (prepared with a high speed stirrer, Ultra-Turrax T25, in the same solvent as the polymer) and mixed with the high-speed stirrer. The films ($\geq$60 μm) were prepared by drawing (draw blade applicator, Industry Tech) the suspensions onto polymer substrates (PET). The performance of the films was determined by irradiation with a diode laser (SDL, XC30) and a specially developed torsion balance (sensitivity as low as 10^{-10} N s) described in detail elsewhere [12]. The decomposition temperature and enthalpy of the polymers were measured with a DSC (Perkin-Elmer DSC 7) under N_2 with heating rates from 10 to 20 K min^{-1}.

3. Results and discussion

3.1. Micro-optical elements: UV-irradiation

The phase masks were designed for 308 nm as irradiation wavelength using an 80 mm focal length projection lens at demagnification factors between 2 and 4. The grating pitch was kept constant at 3 μm, which provides a sufficiently high deflection angle of the diffracted light. The zero order efficiency of the phase mask can be calculated by simple scalar diffraction theory and depends on the duty cycle. The



Scheme 1. Chemical structures of the polymers: triazene-polymer (left) and polyvinylalcohol (right).

duty cycle is defined as the ratio between the spacing of the grating line widths and the grating period. At a duty cycle of 0.5 the zero order diffraction efficiency is 0, when the depth of the grating structures is matched to give a phase shift of π. The ablation depths were measured after ablation using phase masks with various duty cycles. The ablation depths follow the theory quite well. The 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 [5].

Various structures were ablated into the specially designed triazene-polymers and polyimide. The triazene-polymer is very sensitive to laser ablation at 308 nm, with a threshold of $\approx$25 mJ cm^{-2} and an etch rate of 260 nm pulse^{-1} (with 100 mJ cm^{-2}). Polyimide has a very similar absorption coefficient (100,000 cm^{-1}) but a threshold of 60 mJ cm^{-2} and an etch rate of 61 nm pulse^{-1} (with 100 mJ cm^{-2}). In the case of polyimide, a photothermal ablation mechanism is generally accepted at longer wavelengths [16], while it has been suggested that the triazene-polymer ablation is mainly photochemical [17]. It has been shown that the decomposition products of the triazene-polymer are mainly gaseous [18], which do not contaminate the surface, without modification of the remaining polymer surface [19]. In the case of polyimide and most commercial polymers, solid ablation products and carbonization of the polymer surface has been detected [20]. An example of a Fresnel lens etched into the triazene-polymer and polyimide is shown in Fig. 2. The modified and re-deposited material is clearly visible around the ablated structure of the polyimide (bottom left), but is absent for the triazene-polymer (bottom right). Any surface contamination or modification will deteriorate the performance of the micro-optical elements and render the ablation rates unpredictable. The ablation structures are well defined (shown in Fig. 2, top left), and even arrays of structures (Fig. 2, top right) can be created fast and easily. 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 depth of the structures. The triazene-polymer has an etch rate of about 250 nm pulse^{-1} at a fluence of 100 mJ cm^{-2}, while the polyimide has only an etch rate of about 58 nm pulse^{-1}.

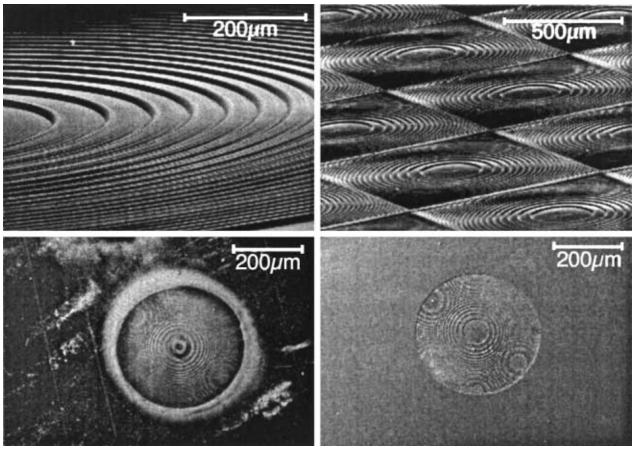


Fig. 2. SEM images of diffractive lenses fabricated by laser ablation: (top) magnification of one lens and array of lenses; (bottom) single lens in polyimide (left, 5 pulses) and in the triazene-polymer (right, 5 pulses).

The combination of gray tone phase masks with the highly sensitive photopolymers is suitable for the fast fabrication of three-dimensional topographies. Single laser pulses can create complex structures such as Fresnel lenses. A pattern transfer into glass or quartz, e.g. by proportional etching techniques, would open an even larger spectrum of applications.

3.2. Laser plasma thruster: near-IR irradiation

To analyze the performance of the polymer films for LPTs, the target momentum was measured by the torsion balance and used to calculate the momentum coupling coefficient, C_{m}. This quantity is defined as

$$C_{\mathrm{m}} = \frac{m\Delta v}{W}$$

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

$$C_{\mathrm{m}}Q^* = v_{\mathrm{E}} = I_{\mathrm{sp}}g$$

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

A scheme of an envisioned design for the LPTs is shown in Fig. 3. Two geometries are possible, i.e. reflection mode, which has the advantage of two times higher I_{sp} and C_{m}, but the disadvantage of an awkward geometry which requires additional shielding for the optical components. The transmission mode has a better geometry and protected optics, but the disadvantage of a two times lower I_{sp} and C_{m}.

The measurements were performed in the transmission mode, which is the most probable candidate for LPTs. PET was chosen as substrate with a thickness of >25 μm. With thinner substrates, a negative momentum was observed due to a burnthrough of the substrates. This was not observed for uncoated PET even at higher fluences. Therefore, it can be assumed that the carbon-doped polymer starts to decompose at the interface to the PET, causing also the decomposition of the PET. If the substrate burns through faster than the coated polymer, a negative momentum will be detected. This was confirmed by holes in the PET after these experiments. Therefore thicker PET substrates ($\approx$100 μm) were applied. Two polymers were selected for the tests, i.e. a polymer designed for laser ablation (triazene-polymer) in the UV and a commercial polymer (polyvinylalcohol). Both polymers pass the fundamental requirements for LPTs. The polymers

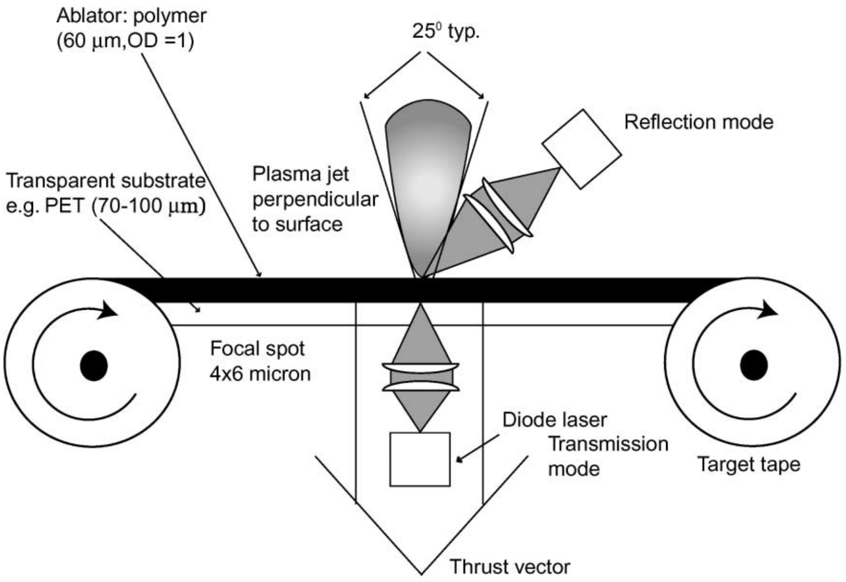


Fig. 3. Scheme of the possible design for LPTs.

give homogenous films with a good adhesion on PET; 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 homogenously 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 around 60 μm. The film thickness is the upper limit which can be accomplished for these polymers by our preparation method and tools.

In Fig. 4, the momentum coupling coefficients at various laser fluences of the carbon-doped triazene-polymer and of a carbon-doped PVAlc are shown. The triazene-polymer reveals higher coupling coefficients and, more importantly, a quite well-defined threshold for a maximum C_m. In Fig. 5 the specific impulses, I_sp, at various laser fluences are shown. The carbon-doped triazene-polymer clearly reveals a higher specific impulse than the polyvinylalcohol. The fewer data

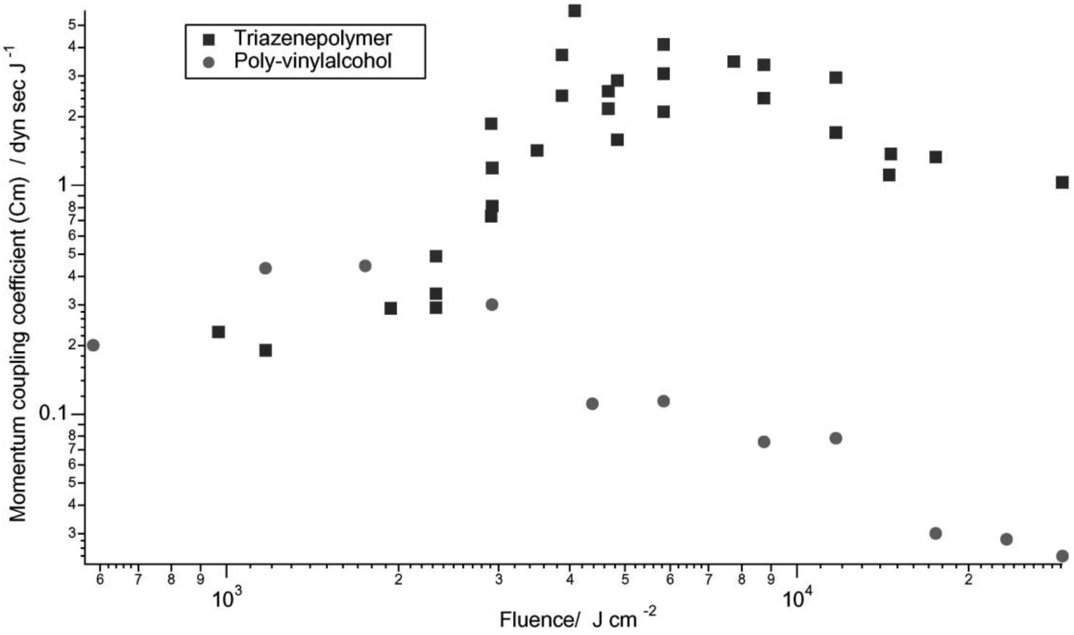


Fig. 4. Momentum coupling coefficients (impulse/laser energy) at various fluences for the carbon-doped polymers. Optical density at 935 nm ≈ 0.9, film thickness ≈65 μm, PET substrates.

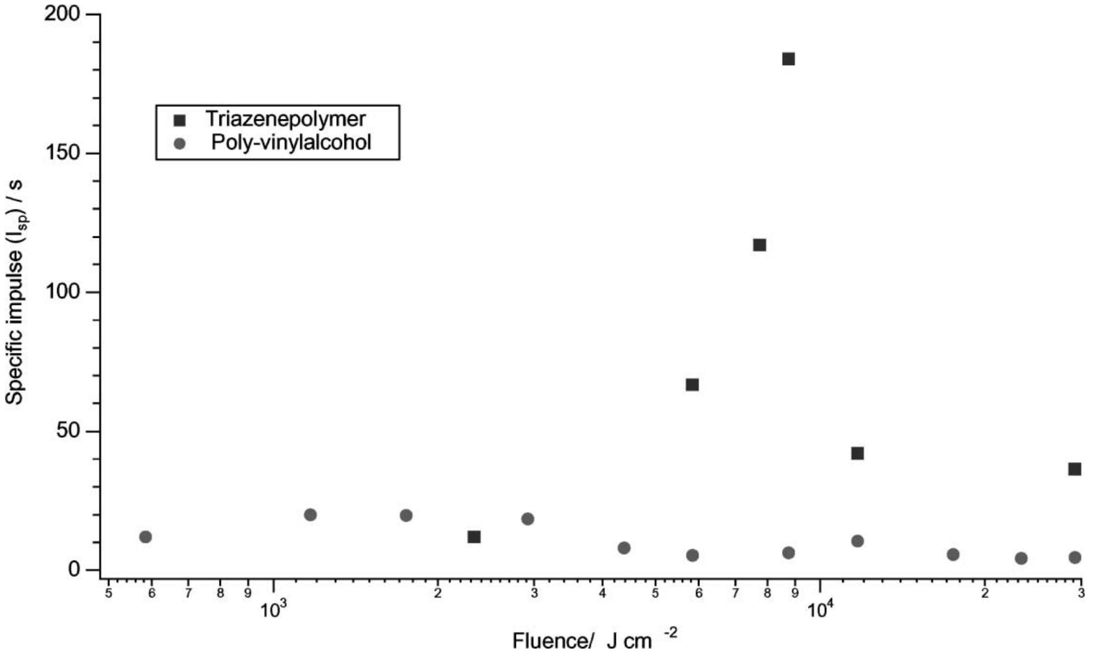


Fig. 5. Specific impulse at various fluences for the carbon-doped polymers. Same materials as in Fig. 4.

points for the triazene-polymer are due to the very irregular shape of the craters which did not allow measurements of the ablated volume at all laser fluences. The I_{sp} values are clearly higher for the triazene-polymer, and probably reveal a threshold at a similar fluence range as for C_m.

The well-defined threshold and higher C_m of the triazene-polymer is an important feature for the design of a plasma thruster with tape-like polymer fuel, because the optimum incident laser fluence and tape speed are clearly defined. The decreasing values of C_m after the maximum are due to the increasing fraction of incident laser energy devoted to accelerating vapor, then creating plasma and to absorption of the laser energy by the created plasma [21]. The well-defined threshold and higher values are probably due to the decomposition properties of the triazene-polymer. The thermal decomposition, initiated by absorption of the laser energy by carbon, follows most probably the same pathway as the UV laser-induced decomposition. The N_3-group is the photolabile group in the polymer, and also the primary decomposition site of thermolysis, as suggested by product analysis by mass spectrometry. In thermolysis, the triazene-polymer exhibits a well-defined, quite sharp (FWHM $\approx$ 60°C) decomposition temperature ($\approx$227°C) and an exothermic decomposition enthalpy ($\approx -0.7\,\mathrm{kJ\,g^{-1}}$) while the PVAlc exhibits a very broad (FWHM $\approx$ 200°C) decomposition peak centered around 260°C. The decomposition is also exothermic ($< -0.5\,\mathrm{kJ\,g^{-1}}$), but the enthalpy could not be determined exactly due to the sloping, ill-defined baseline of the DSC scans. Whether the amount of released energy, the maximum temperature or the width of the decomposition process are more important for creating a threshold for a maximum C_m is not clear at the moment.

If the thermally induced decomposition follows the same pathway as the UV laser-induced decomposition, then it could be possible to select the polymers for LPTs according to similar principles as for UV laser ablation. The most important design features for polymers designed for UV laser ablation are: an exothermic decomposition into gaseous products; well-defined primary decomposition sites in the polymer main chain; and a high absorptivity at the irradiation wavelengths. In future experiments these assumptions will be tested.

4. Conclusion

The combination of phase masks and specially designed highly sensitive photopolymers can be used to fabricate fast three-dimensional topographies using laser ablation. The improvements of the phase mask design, by incorporating the ablation behavior of the polymer into the mask design, and the application of photopolymers, which decompose without contamination of the surface, allows a fast fabrication of micro-optical elements.

The designed polymers also reveal superior properties for applications in the near-IR. The carbon-doped triazene-polymer shows higher values of C_m and I_{sp} as compared to a commercial polymer (PVAlc). The well-defined threshold for the momentum coupling coefficient is an important aspect for the application of polymers in laser plasma thrusters.

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