Characterisation of combined positive-negative photoresists by excimer laser ablation

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Abstract. Novel photopolymers containing side groups based on o-methoxycinnamylidenemalonic acid, which undergo selective photo-crosslinking without destruction of the polymer backbone upon irradiation at $\lambda > 395$ nm, have been developed for potential applications as combined positive-negative resists and multilayer resists. An XeCl excimer laser ($\lambda = 308$ nm, $\tau = 20$ ns) was used as the irradiation source to study the ablation and microstructuring characteristics of the polymers. The materials were structured before and after crosslinking. The ablation rate was analysed by varying the fluence (0.01–10 J/cm^2) and the number of pulses for a given irradiation area. Etch rates of about 2 µm per pulse at a fluence of 9 J/cm^2 could be achieved for all polymers. The polymer with triazene groups reveals a higher etch rate at low fluences (less than 300 mJ/cm^2) than the polymer without a triazene group. The experimentally observed threshold fluence for the triazene-containing polymer is about 30 mJ/cm^2. Using a Schwarzschild-type reflection objective (15×), microstructures with a resolution in the micron range were produced on both polymer films. The quality of the structures was evaluated by scanning electron microscopy. The results indicate that the new polymers could be used as resists for excimer laser ablation lithography.

The development of novel photoresists for specific laser irradiation wavelengths is essential for laser structuring in a manufacturing environment, e.g. the electronics industry. These resists must be highly sensitive for high-resolution patterning at the irradiation wavelength, and they must also exhibit other properties, i.e. mechanical, thermal and chemical stability for all additional manufacturing steps. Triazene-containing polymers have been demonstrated to be suitable for laser ablation lithography [1−3]. Several polyesters also exhibit good ablation behaviour [4, 5]. Introducing a functional group that enables selective photo-crosslinking without

destruction of the polymer backbone can form new photoresists, which can function as positive as well as negative resists. An application could be envisioned where first 'large-scale' structuring, using standard negative resist methods, is followed by a positive (e.g. laser ablation) step to structure the remaining areas in more detail. In this work, monomers based on o-methoxycinnamylidenemalonic acids were used as photo-crosslinking units. Cinnamylidenemalonic acid is known to photodimerize via $(2 + 2)$-cycloaddition [6]. The photo-crosslinking groups absorb at $\lambda > 395$ nm. At these wavelengths, neither triazene groups nor ester groups are absorbing. The chemical structures of the new polymers TCP3 and CSMP3 are shown in Fig. 1. TCP3 contains triazene functional groups, whereas CSMP3 is a polyester without triazene groups.

1 Experimental

The polymers TCP3 and CSMP3 were synthesised by using a standard polycondensation reaction. The details of the preparation are described elsewhere [7]. The structure and composition of the compounds were determined by ^{1}H and
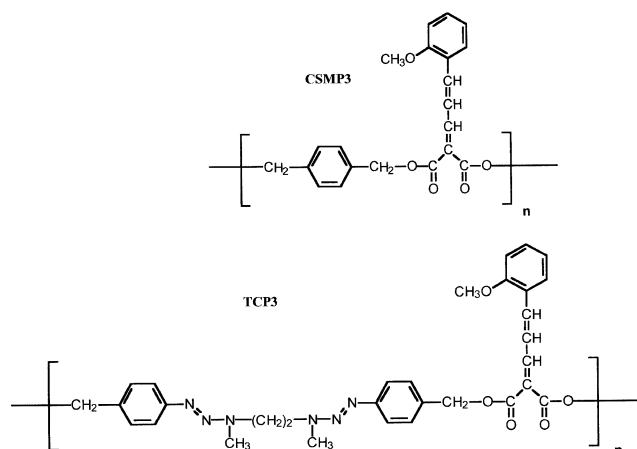
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Fig. 1. Chemical structures of the polymers TCP3 and CSMP3

Table 1. Physical and chemical properties of the polymers

	$M_n/\text{g mol}^{-1}$ [a]	M_w/M_n [b]	$T_g/°C$ [c]	$T_{dec.}/°C$ [d]	λ_{max}/nm	$\alpha_{\lambda(max)}/\text{cm}^{-1}$ [f]
CSMP3	3800	1.5	58.3	328	359 [e]	91 000
TCP3	6500	1.5	61.2	245	316	98 000
CSMP3c	–	–	*	**	354 [e]	**
TCP3c	–	–	*	**	310	**

[a] The number-average molecular weight determined by GPC measurements (solvent THF), M_n
[b] the polydispersity, M_w/M_n
[c] the glass transition temperature determined by DSC measurements (heat rate $10\,\text{K min}^{-1}$), T_g
[d] the decomposition temperature determined by TGA (thermo-gravimetric analysis) measurements (heat rate $10\,\text{K min}^{-1}$), T_{dec}
[e] shoulder at 311 nm
[f] and the linear absorption coefficient at maximum absorption wavelength determined by UV spectroscopy and profilometry, $\alpha_{\lambda(max)}$
* No T_g below 350 °C
** Not determined

^{13}C-NMR spectroscopy. Photo- crosslinking of the polymers was realised by irradiation at $\lambda > 395$ nm for 40 minutes. Infrared spectroscopy was used to confirm crosslinking in the bulk of the polymer films. After crosslinking, the polymers are called TCP3C and CSMP3C, respectively. The properties of the polymers are compiled in Table 1. Polymer films with a thickness of about 50 μm were prepared by solvent casting for the laser ablation experiments.

An XeCl excimer laser (Lamda Physik; $\lambda = 308$ nm, $\tau = 20$ ns) was used as irradiation source in the experiments. 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 $0.001\,\text{J/cm}^2$ and $10\,\text{J/cm}^2$ by using a dielectric attenuator (Laser Laboratorium, Göttingen) and an additional beamsplitter (10% transmission). The number of pulses delivered to the sample was controlled by a pneumatic shutter. For a typical experiment, a 10×10 matrix of circular craters was created on every polymer film while the fluence and the pulse number were varied. The depth of the ablated craters was measured with a surface profiler (Dektak 8000).

For the microstructuring experiments, a copper mask (diameter $= 3$ mm) with a slit pattern was used. The mask consists of two different slits with widths of 100 and 60 μm. The mask was imaged by a Schwarzschild-type reflecting objective (Ealing, demagnification 15×) onto the polymer surface to avoid lens aberration. The quality of the ablated structures was evaluated by scanning electron microscopy (SEM).

2 Results and discussion

Thin polymer films were cast on quartz plates to measure the UV and visual spectra. The UV spectra were measured before and after photo-crosslinking, as shown in Fig. 2. CSMP3 has an absorption maximum around 359 nm, probably due to the absorption of the photo-crosslinkable group. The absorption maximum of TCP3 at 316 nm is the superposition of the triazene group and crosslinking functional group. Triazene-containing polymers without conjugated double bonds are known to have an absorption maximum around 300 nm [1, 2]. Figure 2 shows that photo-crosslinking decreases the absorp-

tion in the region close to the absorption maximum. A series of polymer films with different thickness were prepared for the determination of the linear absorption coefficients ($\alpha_{\lambda(max)}$ and $\alpha_{\lambda(308)}$) of the polymers. The results are given in Tables 1 and 2. TCP3 exhibits a higher absorption coefficient at 308 nm (laser wavelength) than CSMP3 does, which may affect the ablation behaviour.

The etch rates of the polymers were calculated from plots of etch depth versus pulse number as shown in Fig. 3a for TCP3C. Ablation parameters, α_{eff} (effective absorption coefficient) and F_{th} (threshold fluence) were fitted according to

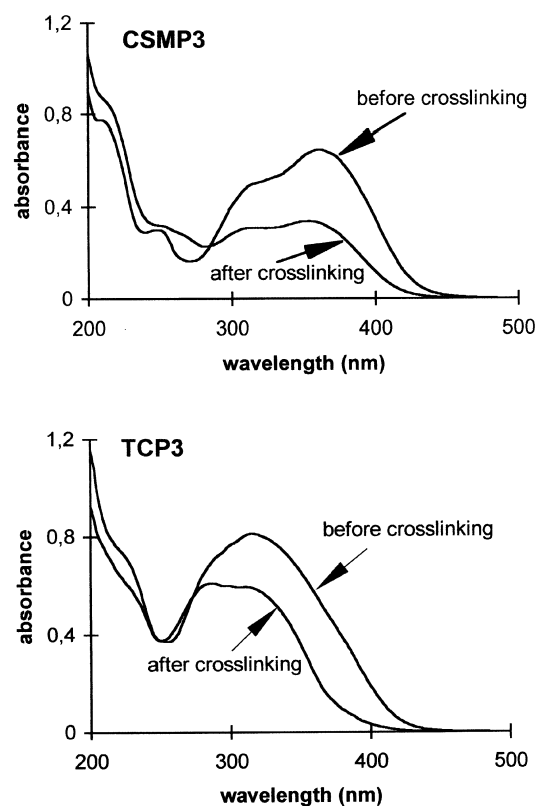$$d = \frac{1}{\alpha_{eff}} \ln\left(\frac{F}{F_{th}}\right), \tag{1}$$

Fig. 2. UV spectra of the polymer films before and after cross-linking

Table 2. Ablation parameters of the polymers

	$\alpha_{\lambda(308)}$ (cm^{-1})	α_{eff} [c] (cm^{-1})	F_{th} [d] (J/cm^2)	observed F_{th} [e] (J/cm^2)	d(μm/pulse) at 0.158 J/cm^2	d(μm/pulse) at high fluence
CSMP3	65 000 [a]	29 000	0.080	0.043	0.251 ± 0.003	1.78 ± 0.38 at 8.3 J/cm^2
CSMP3C	42 000 [b]	28 000	0.086	0.043	0.224 ± 0.002	1.88 ± 0.19 at 8.4 J/cm^2
TCP3	96 000 [a]	26 000	0.064	0.032	0.343 ± 0.003	2.10 ± 0.32 at 8.8 J/cm^2
TCP3C	71 000 [b]	*	*	*	*	2.15 ± 0.37 at 8.8 J/cm^2

[a] linear absorption coefficient at 308 nm determined by UV spectroscopy $\alpha_{\lambda(308)}$
[b] linear absorption coefficient at 308 nm determined by UV spectroscopy after photocrosslinking $\lambda > 395$ nm, $t = 40$ min
* Not determined
[c] the effective absorption coefficient α_{eff} calculated from (1)
[d] the threshold fluence F_{th} calculated from (1)
[e] and the observed F_{th}, defined as the lowest fluence at which ablated craters can be observed with a microscope
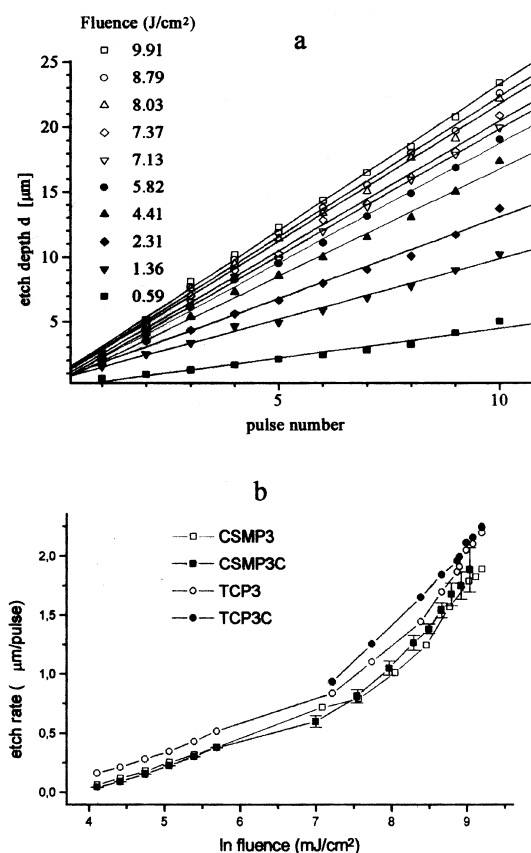

Fig. 3. a Plot of the etch depth as a function of the pulse number for TCP3C. **b** Etch rates versus natural logarithm fluence for all polymers. Typical error bars of the measurements are shown for CSMP3C

where d is the etch rate (etch depth per pulse) [8]. Table 2 summarises the resulting values of α_{eff}, F_{th} and the etch rates at several fluences and the *observed* threshold fluences, defined as the lowest fluence at which ablated craters can be observed with a microscope. A plot of the etch rates versus the natural logarithm of the fluence is shown in Fig. 3b for all polymers, revealing a linear relation in the low-fluence range. The results in Table 2 and Fig. 3b reveal that at high fluence ($F > 0.5$ J/cm^2) the etch rates of TCP3 and TCP3C

are slightly higher than those of CSMP3 and CSMP3C. However, the difference between the etch rates TCP3 and CSMP3 is more pronounced at low fluences ($F < 0.3$ J/cm^2), suggesting that the triazene-containing polymer TCP3 has a higher ablation sensitivity probably due to its higher linear absorption coefficient at the irradiation wavelength (see Table 2). The calculated effective absorption coefficient α_{eff} is lower for TCP3 than for CSMP3 and CSMP3C. The measured linear absorption coefficients of the polymers are much higher than the effective absorption coefficients calculated from (1) (Table 2). The maximum etch rate of these polymers is ≈ 2 μm/pulse at ≈ 9 J/cm^2. Obviously, the calculated threshold fluence does not agree with the observed value, probably because the data deviate from (1) at high fluences (see Fig. 3b). It is known that this equation is only valid over a small range of fluences [9]. The observed threshold fluences of the polymers, ≈ 30 mJ/cm^2 for TCP3 and ≈ 40 mJ/cm^2 for CSMP3, are quite low, which is important for potential applications. After crosslinking, a three-dimensional network is formed resulting in a higher mechanical strength and higher thermal stability. However, crosslinking has little effect on the etch rates, the effective absorption coefficient and threshold fluence. This could be a function of the degree of crosslinking, which is not determined at the moment.

The main difference of the two polymers TCP3 and CSMP3 used in this study is that the former contains triazene groups. The linear absorption coefficient of TCP3 is higher than that of CSMP3 (Table 1,2), but this does not result in a significant difference in the etch rates at high fluences. The lack of correlation between ablation rate and absorption at high fluences for polymers has been ascribed to non-linear effects and to the absorption by laser-induced plasma [10]. However, the triazene-containing polymer, TCP3, exhibits a higher sensitivity to laser irradiation at low fluences, although more experiments using various triazene-containing polymers are needed to clarify this point. It is not surprising that the polyester CSMP3 exhibits good ablation behaviour too. Actually, good ablation behaviour has been reported for several polyesters without photo-crosslinking groups [4, 5].

For triazene-containing polymers, e.g. TCP3, the absorption of photons leads to the excitation of the triazene chromophore, resulting in the decomposition of the chromophore and the release of nitrogen. The removal of solid fragments,

formed during laser ablation, can be facilitated by the released nitrogen which acts as a driving gas. The decomposition of the triazene functional group during laser irradiation has been shown by measuring the UV spectra of a triazene-containing polymer after irradiation [11] and by measuring the transmission of the pulse [12]. In the case of CSMP3, ester groups are suggested to be the chromophore [4, 5]. The scission of the CO–O bond produces a gaseous product, e.g. CO and CO_2, which can act as driving gases in this case.

The surface features in the ablated area of the polymer films are characterised by SEM. At high fluences, well-defined circular craters with diameters of about 0.28 mm are observed, as shown in Fig. 4a. The circular structures on TCP3C films exhibit sharp edges and a smooth bottom surface. Similar structure qualities are observed on all polymer films, suggesting that, at least at high fluences, the triazene group does not play an important role for the quality of the ablated structures. At low fluences ($F < 300 \ mJ/cm^2$), however, some differences are observed. Increasing pulse numbers results in deep craters; for the polymers TCP3, TCP3C and CSMP3, conical structures were formed during laser ablation (shown in Fig. 4b), whereas smooth bottoms were observed for CSMP3C. The heights of the cones, shown in Fig. 4b, are greater than $10 \ \mu m$. The densities and sizes of the cones are dependent on the fluence and pulse number. Fewer cones were formed at higher fluences and with fewer pulses.

Conical structures, as shown in Fig. 4b, have been observed after ablation of, for example, polyimide [13], one triazene-containing polymer [11] and polyaniline [14]. The structures formed on different polymer surfaces appear quite similar. The formation of such cones can shield the ablation of the underlying polymer and even stop the ablation at a given fluence [15]. Possible mechanisms, such as selective etching of amorphous and crystalline regions, convection instability in the heated surface layer, stress relaxation in a molten surface layer and impurities present in the polymer, have been proposed [13], although none can explain all results. Irradiation of polymers with aromatic systems results in carbonization of the polymer surface. This carbon-containing layer can
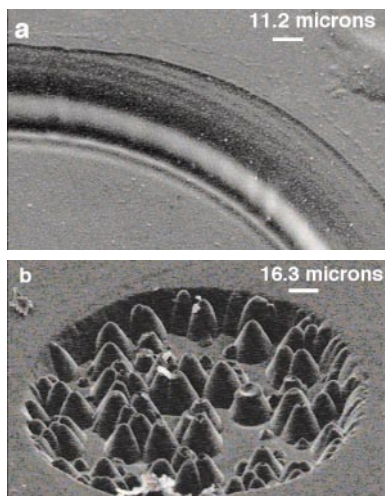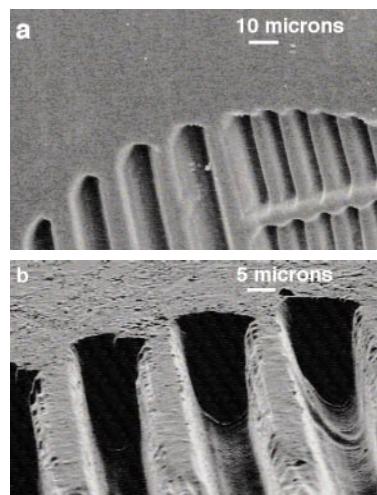

Fig. 5a,b. SEM micrographs of microstructures. **a** Created on CSMP3 at $7.9 \ J/cm^2$ with 7 pulses. **b** Created on TCP3C at $5.6 \ J/cm^2$ with 9 pulses

even consist of microcrystalline graphitic structures [16], which have different threshold fluences than the polymers. This might result in the previously described shielding effect and therefore the formation of the observed cones. However, this kind of cone was not observed on the CSMP3C film even at very low fluences. It is surprising that CSMP3 and CSMP3C exhibited different behaviour at this point. Further experiments with different polymers are needed in order to explain this result.

To demonstrate the possibility of high-resolution patterning, microstructures with channel patterns are created (see Fig. 5). Well-defined patterns with sharp edges, steep slopes and flat bottoms are achieved. The resulting patterns consist of broad (ca. $8 \ \mu m$ wide) and narrow (ca. $4 \ \mu m$ wide) channels. The depth of the channels in Fig. 5b is greater than $10 \ \mu m$. Microstructures produced on the films of TCP3 and CSMP3 exhibit similar qualities. The resolution achieved in this study is limited by the experimental set-up, not by the polymers. Microstructures with sub-micron resolution could probably be created on the polymers by improving the optics. In fact, a resolution of $0.4 \ \mu m$ was achieved on one triazene-containing polymer by using a different set-up [2].

3 Conclusion

The laser ablation behaviour of potential positive-negative resists, TCP3 and CSMP3, has been investigated at low and high fluences. The presence of the triazene functional groups increases the sensitivity of the polymers to laser ablation at low fluences, probably owing to the higher linear absorption coefficient. Well-defined microstructures can be created on the polymer films at high fluences, whereas conical structures were formed on the ablated surfaces of TCP3, TCP3C and CSMP3 films during ablation at low fluences, reducing the quality of the ablated structures. In contrast, no cones were observed for the crosslinked polymer CSMP3C, which contains no triazene groups. The crosslinking has only minor effects on the ablation behaviour with given crosslinking parameters. Additional work is needed to study the role of triazene functional groups on the ablation behaviour. In order

Fig. 4a,b. SEM micrographs of the resulting structures. **a** TCP3C irradiated at $10 \ J/cm^2$ with 9 pulses. **b** TCP3 irradiated at $43 \ mJ/cm^2$ with 200 pulses

to avoid conical structures on the ablated surfaces at low fluences, further studies on the formation mechanisms are needed.

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