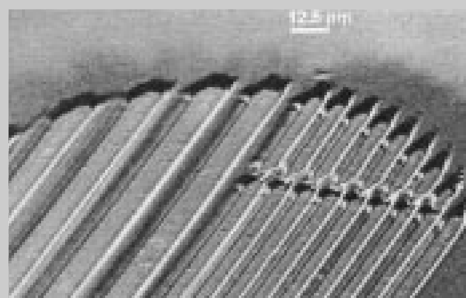
Full Paper: Novel photopolymers, based on cinnamylidenemalonyl groups, were designed for excimer laser ablation lithography. These polymers are highly sensitive to laser ablation at a specific irradiation wavelength, i.e., 308 nm, but can also be applied as classical, negative photoresist. The crosslinking of the polymer is accomplished by irradiation at >395 nm. The sensitivity of the photopolymers to laser ablation before and after crosslinking is nearly equal. The combination of these two processes, i.e., laser ablation and photocrosslinking, can be applied for the fabrication of arrays of microstructures. The laser ablation step is used to fabricate microstructures, while the classical wet processing is used for large area structuring. Combined processes of crosslinking-wet development and laser microstructuring, but also vice versa were carried out. The microstructures had the same high resolution, independent of the processing order.



SEM picture of the CM polymer after inverse processing, i.e., first laser structuring, then crosslinking and wet development.

Development and structuring of combined positive-negative/negative-positive resists using laser ablation as positive dry etching technique

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Introduction

Laser ablation or dry etching is an advanced, fast method for direct structuring of polymers, with less processing steps compared to the standard lithography methods, but has unfortunately several disadvantages, i.e., low sensitivity and carbonization of the substrate.[1] Commercial polymers are not designed for laser dry etching, and it is difficult to evaluate the potential of this technique by using standard polymers and comparing them to the performance of classical, highly developed photoresists. High resolution structuring could not be obtained with physical doping of standard polymers with low molecular weight compounds.[2] Therefore, ultrasensitive, photolabile polymers were developed for laser ablation at specific irradiation wavelengths, i.e., 308 nm.[3,4] This wavelength was chosen because of the convenience of this wavelength from a practical point of view, i.e., lifetime of the optical components and gas fills of the XeCl excimer laser, and because sub-micron resolution is not necessary for all applications. The designed laser polymers contain photolabile chromophores, i.e., —N═N—X<, with a high absorption coefficient at the irradiation wavelength.[5,6] The polymers exhibit very high sensitivity to the laser irradiation wavelength and decompose into gaseous species,[7] which do not contaminate the surface.[8] With this approach high resolution structuring of the polymer is possible, but the irradiation area is limited by the laser beam size. In a production environment many structures must be fabricated in the shortest possible time and with a minimal use of expensive techniques, e.g., laser photons. A 'pure' laser process would be slow and tedious for the creation of arrays of structures, e.g., micro-lens arrays, on a large substrate. To overcome this limitation, novel photopolymers have been developed which can be used as classical negative (crosslinking) resists, but still exhibit very high sensitivity towards laser direct structuring. These polymers are based on polyesters containing cinnamylidenemalonic acid groups (CM polymers) which undergo photocrosslinking upon irradiation at $\lambda > 395$ nm and laser direct

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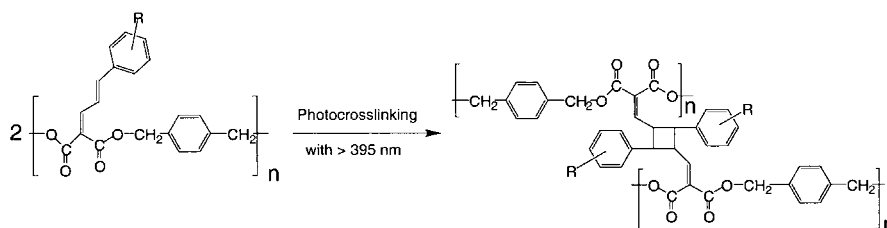

Scheme 1. Structure of the cinnamylidenemalonic ester polymer (CM) before and after crosslinking with $\lambda > 395$ nm for 20 min and 100 mW · cm^{-2}.

structuring at $\lambda = 308$ nm.[9] The CM polymers are also special designed for excimer laser lithography using the XeCl excimer laser (308 nm). The polymers reveal a high absorption coefficient at 308 nm, decompose into gaseous species which do not contaminate the surface, and exhibit a high sensitivity to laser ablation. A benchmark of the sensitivity for an industrial application, which cannot be reached by commercial polymers, is an etch rate of ≥100 nm with an irradiation fluence of 100 mJ · cm^{-2}.[10] The CM polymers are additionally stable to acids which are applied in following processing steps. This stability is unique to the novel designed CM polymers and could not be accomplished by the previously designed polymers.[11] The order of processing, i.e., first negative then positive (–/+) structuring or vice versa (+/–) is not affecting the quality of the structures on a micrometer scale. Such a combined process was to our knowledge only reported once, but for a different and even more complex technique, i.e., ion beam irradiation.[12]

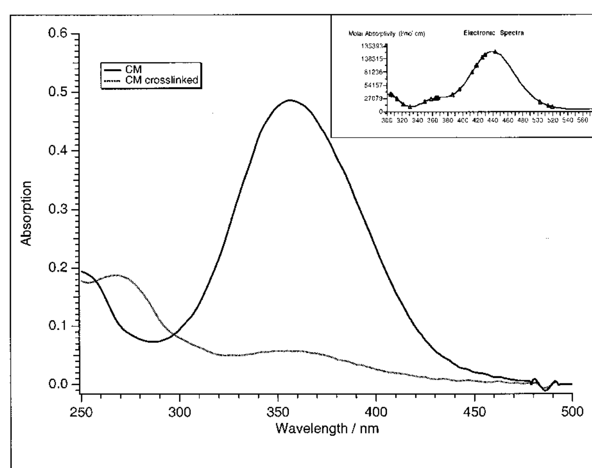

Fig. 1. UV-Vis spectra of the CM polymer (R = p-OCH_3) before and after crosslinking. The insert shows the result of a ZINDO calculation of the UV-Vis spectra of a model repetition unit.

Results and discussion

The structure and crosslinked structure of the CM polymers is shown in Scheme 1. The photo-dimerization, i.e., 2+2 cycloaddition, of cinnamate side-chains[13] is a classical method of polymer photocrosslinking, e.g., used in the KPR® Eastman Kodak resist which has otherwise a very different chemical structure. During crosslinking a cyclobutane system is created, which has a shorter wavelength absorption maximum than the cinnamate group. The UV spectra (R = p-OCH_3) before and after crosslinking are shown in Fig. 1. Semiempirical methods (MOPAC/ZINDO[14]) were used to calculate the absorption spectrum of a repetition unit of the CM polymer. It was derived from the calculations that the absorption maximum in the UV spectrum (at 357 nm) is mainly due to transitions which involve the whole cinnamylidenemalonyl system. The calculated spectrum (ZINDO) is shown as insert in Fig. 1.

The shape of the spectrum is quite similar to the experimental spectrum, but the calculated absorption maximum is shifted to longer wavelengths (by ≈ 80 nm). Several factors will lead to differences between calculated and experimental spectra. The calculated spectra are for gas phase molecules, while the experimental spectra are taken from thin films. This leads to a modification of the molecule's electronic states due to intermolecular interactions. Additionally, model compounds are used for the calculations due to the limited number of atoms allowed in ZINDO. The absorption maximum of the CM polymers can be shifted between 328 and 357 nm by varying the substituent R of the phenyl ring.[15] The synthesis of the CM polymers is described in detail elsewhere.[15] In all following experiments the CM polymer with R = p-OCH_3 is used which allows fast and selective photo-crosslinking of the polymer at $\lambda_{irr} \geq 395$ nm. This results in the development of an insoluble polymer network, but also a reduction of the absorption coefficient, i.e., from 32 000 to 17 000 cm^{-1} at the irradiation wavelength of the XeCl laser (308 nm). The crosslinking rate was not determined in detail but infrared spectroscopic data suggest rates higher than 50%.

The etch rates of the polymer before (CM) and after crosslinking (CM_{cr}) are determined at moderate laser fluences (<500 mJ · cm^{-2}) to test whether crosslinking has a pronounced influence on laser ablation. The comparison of the two etch rates is shown in Fig. 2. A slightly lower etch rate is obtained for the crosslinked polymer. This is probably due to the lower absorption coefficient at the

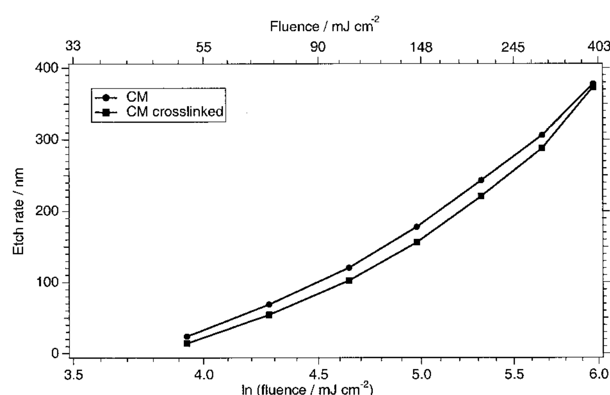

Fig. 2. Ablation rates per pulse, *d*, as a function of the laser fluence *F* for the CM and CM_{cross} polymer.

irradiation wavelength, or less likely to an improved mechanical stability of the crosslinked polymer. One of the most important features of polymer laser ablation is the existence of a sharp threshold fluence for material removal.[16] Below this material dependent laser fluence *no* laser ablation can be observed, while photochemical decomposition/reactions can take place within the polymer film. The threshold fluence, F_0, can be calculated according to Eq. (1)

$$d\,(F) = 1/\alpha_{eff}\,\ln(F/F_0) \qquad (1)$$

where *d* is the etch rate at a given fluence *F* and α_{eff} is the effective absorption coefficient during ablation (different from the linear absorption coefficient obtained from Lambert-Beer's law). The calculated threshold fluences are 48 and 53 mJ · cm^{-2} for CM and CM_{cr} respectively, showing that only slightly higher laser fluences are necessary for the crosslinked polymer. The effective absorption coefficients are more or less the same for both polymers, i.e., 57 000 cm^{-1} for CM and 58 000 cm^{-1} for CM_{cr}. Maximum etch rates of 1.54 μm for CM and 1.54 μm for CM_{cr} can be obtained at high laser fluences, i.e., here 6.3 J · cm^{-2}.

To prove that the concept of combining the characteristics of positive and negative resists (with laser ablation as positive etching) is applicable, a complete combined process was carried out. We would like to emphasize that for this proof of principle, a very simple experimental setup was used and neither the solvent system for the negative development nor the crosslinking parameters were optimized. A brass mask (100 μm thick) with a rectangular pattern was placed on a thin (3 to 5 μm) polymer film on a quartz wafer, cast from $CHCl_3$ as the solvent. This setup is roughly representative of proximity illumination. Then the film was irradiated through the mask pattern with a Xe lamp equipped with a filter $\lambda_{Irr} > 395$ nm for 20 min at a power of 100 mW · cm^{-2}. The irradiated film was developed by immersing CM_{cr} into chloroform for 10 s, which is a good solvent for CM. A scanning electron micro-

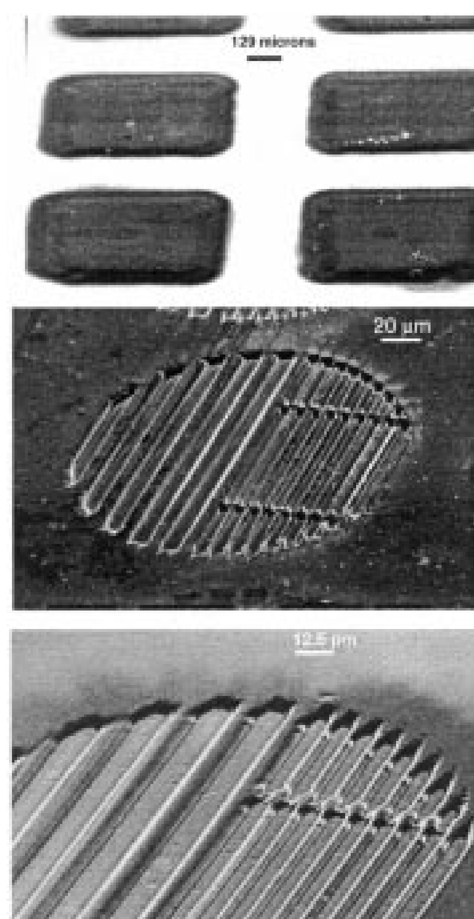

Fig. 3. SEM pictures of the CM polymer after crosslinking. Top: after wet development in $CHCl_3$; middle: structuring of the crosslinked and wet developed polymer (from top SEM) (1 pulse with 7.9 J · cm^{-2} at 308 nm); bottom: inverse processing, i.e., first laser structuring, then crosslinking and wet development.

scope (SEM) picture of the developed, negatively structured film is shown in Fig. 3 (top). The size of the remaining polymer squares is slightly larger than for the mask pattern (520 μm) and also exhibits sloping walls. This is most probably due to the non-optimized experimental conditions, i.e., proximity illumination, illumination time, solvent system and development time. An excessively long illumination time, for example, will cause crosslinking under the mask edges, i.e., widen the crosslinked area, due to multiple reflection between the mask and the polymer surface. The crosslinked polymer squares were subsequently irradiated with a XeCl excimer laser (Lambda Physik Compex 205), through a copper mask with a varying slit pattern, which was demagnified with a reflective objective (Ealing 15 ×). The SEM picture in Fig. 3 (middle) shows the microstructures obtained with a single pulse at 7.9 J · cm^{-2}. Our experimental setup does not allow a precise alignment of the structuring beam. Therefore, multiple structures within

the polymer squares are created. In the upper part of the SEM picture an additional structure is visible. The microstructures, obtained with a single pulses at 7.9 $J \cdot cm^{-2}$, are well resolved and show a resolution close to the limits of our setup (≈ 1 μm). This proofs our concept to combine classical negative resist properties with laser ablation.

To test whether there is a preferential order of processing steps, i.e., first negative development and then positive laser structuring or vice versa, a polymer film was first structured with the laser, then crosslinked and developed in $CHCl_3$. The microstructure (Fig. 3, bottom) reveals the same quality (as far as we can judge from SEM pictures) as the structures obtained for the experiments with the opposite sequence. Of course volume shrinkage upon crosslinking is expected, but was not determined in this study, where only the feasibility of the +/– concept was the aim.

In summary, novel polymers, based on cinnamylidenemalonic acid groups, were designed which combine two key properties for polymer processing: they are highly sensitive to laser ablation at a specific irradiation wavelength and they can act as classical, negative photoresist. The laser ablation step is used to fabricate microstructures, while the classical wet processing is used for large area structuring. After crosslinking the photopolymers exhibit nearly the same high sensitivity to laser ablation. Combined processes of crosslinking-wet development, laser microstructuring, but also vice versa were carried out. No preferential order of processing was found, which clearly proofs the feasibility of our concept, which allows to combine the strengths of both methods.

Acknowledgement: This work was financially supported by the *Swiss National Science Foundation*.

Received: May 2, 2000
Revised: September 22, 2000

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