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Polymers designed for laser microstructuring

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Abstract

Several polymers were tested for an application of laser ablation as an alternative to photolithography. Tailored specialty polymers revealed the highest sensitivity to laser ablation. The most sensitive polymers are based on the photolabile triazene chromophore (–N=N–N<) which is unfortunately also sensitive to other processing steps, e.g. wet etching. Polymers with a cinnamylidenemalonic acid ester group, showed not only a high sensitivity but also stability to wet etching, high quality film-formation properties and high resolution ablation structures. This proves that it is possible to apply laser ablation as alternative technique to photolithography, if the polymers are especially designed for laser ablation.

Keywords: Laser ablation; Polymers; Photopolymers; XeCl excimer laser; Polyimide

1. Introduction

During the last decade laser processing of polymers has become an important field of applied and fundamental research. One of the most promising proposals, to use laser ablation as dry etching technique in photolithography has not yet been developed into an industrial application [1]. Many disadvantages of laser ablation compared to conventional photolithography are the result of the use of standard polymers. These polymers are designed for totally different applications but have to compete with the highly specialized photoresists. Here, a new approach to laser ablation lithography (LAL) will be described: the development of polymers specially designed for high-resolution laser ablation [2]. These polymers (TC-polymers) contain photolabile groups (–N=N–X–) in the polymer backbone which decompose upon laser irradiation. Various functional groups such as X, which are –N<, –S–, –N–N=N–, phosphate have been tested [3]. The triazene-polymers with –N=N–N< as structural unit revealed most of the desired properties, e.g. formation of high quality films, stability to storing and one-step synthesis. The requirements for the application of laser ablation as an alternative technique to classical photolithography are: *sensitivity* (etch rate per pulse at 100 mJ $cm^{-2} \geq 100$ nm), *stability* to 'wet' acid etching, production of high *quality* films by spin coating and *resolution* of the ablation structures of ≤ 1 μm. The TC-polymers, a novel polymer based on a cinnamylidenemalonic acid ester groups (CM-polymers) and polyimide (PI) were tested for the ability to satisfy the previously described requirements.

2. Experimental

The laser ablation experiments were carried out with a XeCl excimer laser with an emission wavelength

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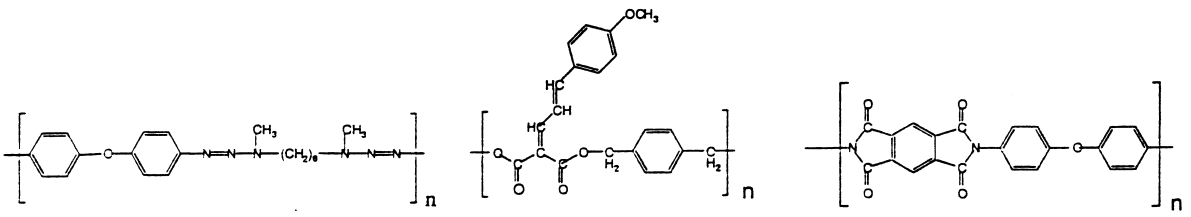

Scheme 1. Chemical structures of the polymers from left to right: TC, CM, PI.

of 308 nm, as described in detail elsewhere [2]. The TC-polymers were synthesized according to [4] and the CM-polymers according to [5]. PI sheets were obtained from Goodfellow. The chemical structure of the polymers is shown in Scheme 1.

3. Results and discussion

The laser ablation characteristics of the polymers, TC-polymer, CM-polymer and PI were studied at high (>0.5 J cm^{-2}) and low fluences. All polymers can be characterized as highly absorbing ($\alpha_{lin} >$ 10 000 cm^{-1}). The relevant physical data are summarized in Table 1. PI was chosen as a benchmark to compare our designed specialty polymers with a well studied, commercial polymer that was not designed for laser ablation. At high fluences no pronounced differences between the polymers are detected. This is not unexpected because the ablation characteristics at high fluences are governed for strongly absorbing polymers, by effects such as plasma absorption and shielding [6]. At low laser fluences pronounced differences between etch rates of the different polymers are detected. The data in Fig. 1 were analyzed according Eq. (1)

$$d(F) = \frac{1}{\alpha_{eff}} \ln\left(\frac{F}{F_0}\right) \quad (1)$$

Table 1
Physical and ablation data of the various polymers

	TC-polymer	CM-polymer	Polyimide
α_{lin} (cm^{-1})	116000	32000	95000
α_{eff} (cm^{-1})	50000	57000	83000
F_0 (mJ cm^{-2})	27	48	60
d(100 mJ cm^{-2}) (nm)	267	128	61
d(10 J cm^{-2}) (μm)	2.1	1.88	1.89

where d(F) is the etch rate per pulse at a given laser fluence (F), α_{eff} is the effective absorption coefficient during ablation (different from the linear absorption coefficient α_{lin}, obtained according to Lambert–Beer) and F_0 is the threshold fluence. The parameters calculated from the fits are listed in Table 1.

The etch rates at a given fluence are obtained from the slope of linear plots of the etch depth versus the number of pulses delivered at a given fluence. For all polymers linear relations were obtained. A comparison of the etch rates per pulse at low fluences for the different polymers is shown in Fig. 1.

The TC-polymer reveals the highest etch rates and lowest threshold fluence, followed by the CP-polymer and PI. The detailed analysis of the data in Table 1 confirms that the designed polymers (TC and CM-polymers) pass the *sensitivity* criterion, while PI fails. The difference in the etch rates between the TC and CM-polymer can be explained by the higher photochemical activity of the TC-polymers (in solution more than a factor of 2). The *resolution* of the ablation structures for all polymers is within the desired limits (SEM analysis of microstructures created with a high resolution setup, described in detail in [2]) but in the case of PI carbonization inside the ablation zone and in the vicinity of the ablation zone, due to re-deposition of ablation products was detected [7]. The designed polymers decompose mainly into gaseous products which do not contaminate the surface after ablation [3]. The *quality* of the films is also sufficient. For solvent-cast films average roughnesses from 8 to 10 nm are detected with a profilometer (scan length 100 μm), while for a spin-coated TC film a roughness of 1.5–2.0 nm were detected by atomic force microscopy (scan length 10 μm) [8]. As a last test the *stability* of the tailored polymers to wet 'acid' etching is examined. A thin polymer film was immersed into a HNO_3 (42 wt.%)/HCl (3.6 wt.%)/H_2O (54.4 wt.%)

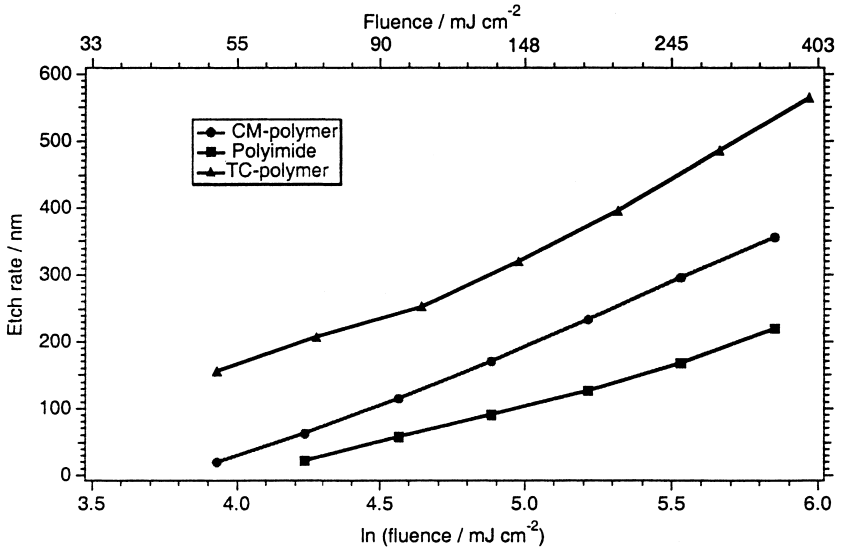

Fig. 1. Etch rates vs. laser fluence of the various polymers.

mixture for 1 min and UV–VIS spectra were recorded before and after immersion. The TC films decomposed totally, while the CM-polymer films exhibited almost no changes in the spectra. This shows that the CM-polymers are stable under wet 'acid' conditions and therefore pass the *stability* criterion. The CM-polymer thus emerges as satisfying all criteria for LAL.

4. Conclusions

Several polymers were tested for an application of laser ablation as an alternative to a photolithographic process. Those polymers which were especially designed for laser ablation, revealed a higher sensitivity than a commercial polymer with a similar absorptivity. The most sensitive polymers are based on the triazene chromophore (–N=N–N<) which is unfortunately also sensitive to subsequent processing by wet etching. The polymers based on the cinnamylidene-malonic acid ester group, by contrast not only showed a sufficiently high sensitivity but also stability to wet etching, high film forming and ablation quality. This proves that it is possible to apply laser ablation as an alternative photolithographic technique, if the polymers are especially designed for this application.

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