Title:

PHOTOPOLYMERS DESIGNED FOR HIGH
RESOLUTION LASER ABLATION AT A SPECIFIC
IRRADIATION WAVELENGTH.

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Photopolymers designed for high resolution laser ablation at a specific irradiation wavelength

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ABSTRACT

We have developed novel photopolymers based on the triazeno chromophore group. The absorption properties can be tailored for a specific irradiation wavelength (e.g. 308 nm XeCl laser). With the introduction of a photolabile group into the main chain of the polymer we expected a mechanism which is mainly photochemical. This should result in high resolution etching with no thermal damage or chemical / physical modification to the material. The gaseous products of the photochemical decomposition were thought to assist the material removal, and to prevent the re-deposition of solid products which would contaminate the surface. We confirmed (SEM/AFM) that the irradiation of the polymer at 308 nm resulted in high resolution etching. No debris has been found around the etched corners. Maximum ablation rates of about 3 μm / pulse were achieved due to the dynamic absorption behavior (bleaching during the pulse). No physical or chemical modifications of the polymer surface could be detected after irradiation at the tailored absorption wavelength, whereas irradiation at different wavelengths resulted in modified (physical and chemical) surfaces. The etching mechanism can be described as a laser induced microexplosion, revealed by ns-imaging. The etching of the polymer starts and ends with the laser pulse, shown by ns-interferometry, confirming that the acting mechanism is mainly photochemical at high fluences for our polymers. Our results demonstrate that the mechanism of ablation can be controlled by designing special polymers, which can be used as high resolution laser dry etching resists.

Keywords: Photopolymer, laser ablation, mechanism, excimer laser, triazenopolymer

1. INTRODUCTION

In recent years excimer lasers have been successfully applied to structuring photopolymers: one particular application is the dry etching of resists in microlithography¹, due to the higher achievable resolution and the lower amount of used solvents. One of the most important problems in laser polymer ablation is the active mechanism. There are two main mechanisms for the first step of ablation: photochemical and photothermal². A photochemical mechanism will, in principle, result in a higher resolution and a less complex pathway of decomposition. It has also been suggested that gaseous ablation products are able to support the dry etching process as carrier gas for solid products. These products can be re-deposited on the polymer surface and result in additional cleaning steps³.

In our project we planned to combine the advantages of a photochemical decomposition pathway with the release of gaseous products. In previous studies we developed various photopolymers⁴ and focused on the most promising candidate: a polymer with two triazengroups per repetition unit⁵. The structural formula is shown in chart 1. The photochemical as well as the thermal properties of these polymers can be controlled by varying R_1 to R_3 ⁶. The absorption maximum can be shifted between 290 and 380 nm, whereas the glass transition temperature ranges from 33 to 110°C,

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and the decomposition temperature from 220 to 300°C (both measured with Differential Scanning Calorimetry). All polymers are soluble in standard solvents, can be decomposed (stripped) with aqueous acidic solution, and give high quality films, using spin coating or solvent casting techniques.

Here we report the results from a combination of techniques to test the potential of these polymers and to study the acting mechanism. We applied static measurements, such as scanning electron microscopy (SEM), atomic force microscopy (AFM), profilometry (etch depth) and surface analysis techniques (XPS), such as contact angle and x-ray photoelectron spectroscopy, after irradiation. In addition we used dynamic techniques during the irradiation, such as laser transmission, ns- photography and ns-interferometry.

2. EXPERIMENTAL SETUP

The polymers were synthesized by an interfacial polycondensation as reported elsewhere^{6b,7}. Due to the different laser equipment for the various experimental set-ups two different polymers have been used. For both polymers $R_2 = \text{CH}_3$ and $R_3 = \text{C}_6\text{H}_{12}$. For the ns-photography and interferometry experiments $R_1 = \text{m-SO}_2$ and the irradiation source was a XeF (351 nm) excimer laser. For all other experiments a polymer with $R_1 = \text{p-O}$ and a XeCl (308 nm) or a KrF (248 nm) excimer laser have been used. Both, the 308 and 351 nm irradiation are close to the absorption maximum of the polymers, and result in an excitation of the $\pi\text{-}\pi^*$ transition of the triazengroup⁸. The experimental set-up for high resolution experiments⁹, transmission experiments⁸, ns-photography¹⁰ and ns-interferometry¹¹ have been reported previously.

3. RESULTS AND DISCUSSION

Fig. 1: Dependence of the etch depth / pulse on the laser fluence

1. Etch rate and quality

The etch rate was measured after irradiation at 248 or 308 nm. The data are shown in Fig. 1. Irradiation at 308 nm, corresponding to the *higher* absorption coefficient as compared to 248 nm, results in a *higher* etch rate. This gives the first indication that excitation of the photolabile chromophore at 308 nm, instead of the excitation of the phenyl groups at 248 nm, can change the acting mechanism. The maximum achievable etch rate of about 3.2 $\mu\text{m} / \text{pulse}$ is also higher than has been observed for most other neat polymers (e.g. polyimide 2 $\mu\text{m} / \text{pulse}$). The SEM picture (Fig. 2) shows a clean ablation crater, with no pronounced damage to the side walls and no re-deposited products. This demonstrates that the concept of combining photolabile groups in the polymer main chain, which results in gaseous decomposition products, can lead to the application of laser polymer ablation as a "true" dry etching technique. The achievable resolution was studied using AFM.

Fig. 2: SEM-micrograph of ablated triazenopolymer; diameter: 290 microns, 5 pulses: fluence 7.5 J cm^{-2} .

Fig. 3: AFM-micrograph of ablated triazenopolymer; 1 pulse: fluence 7.5 J cm^{-2} .

A copper mask was imaged by a reflection objective onto the sample surface, using a single pulse with a fluence of 7.5 J cm^{-2} . The resulting AFM micrograph is shown in Fig. 3. The etch depth and width of the ridges are in good agreement with the expected values. The smoothed edges are partly a result of the AFM imaging but also suggest some thermal effects of the ablation mechanism.

For a detailed understanding of the active mechanism, the polymers have been studied after irradiation with 248 and 308 nm using SEM, contact angle, and XPS measurements.

2. Surface analysis

Fig. 4: Changes of the water contact angle after irradiation with fluences below the threshold energy of ablation. Irradiation with various pulse numbers at 248 and 308 nm.

Fig. 5: SEM-micrograph of surface changes: after 250 pulses with 36 mJ cm^{-2} . Diameter of the naps: $\approx 4 \mu\text{m}$.

Fig. 6: Atomic ratios in % of the triazenopolymer after irradiation with various pulse numbers with 36 mJ cm^{-2} at 248 nm.

Fig. 7: Atomic ratios in % of the triazenopolymer after irradiation with various pulse numbers with 30 mJ cm^{-2} at 308 nm.

Thin films of the polymer were cast on quartz or glass wafers. The polymers films were irradiated at 248 and 308 nm (absorption coefficients: 166000 cm^{-1} at 308 nm and 66000 cm^{-1} at 248 nm) corresponding to a maximum and minimum of absorption. Fluences above (32 mJ cm^{-2} at 248 nm and 22 mJ cm^{-2} at 308 nm) and below the threshold of ablation (9 mJ cm^{-2} at 248 nm and 10 mJ cm^{-2} at 308 nm) ^{8,12} have been applied.

The polymer surface was modified selectively with different laser irradiation wavelengths. The two laser energy regimes, above and below the threshold for laser ablation, reveal pronounced differences. For both irradiation wavelengths (248 and 308 nm) the polymer surface modification is solely chemical after treatment with fluences below the threshold. Each

irradiation wavelength leads to a surface oxidation, as shown with the contact angle (Fig. 4) and XPS measurements. The oxidation is a result of the radical pathway of photo decomposition of the triazeno chromophore¹³.

At fluences above the ablation threshold a different behavior is observed for each wavelength. After irradiation with 248 nm, growing "nap" like structures are detected, shown by the SEM picture in Fig. 5, possibly a result of crosslinking of the polymer, as indicated by insoluble residues after irradiation. The surface appears black and carbonized, shown by the change of the atomic ratios in the XPS spectra (Fig. 6), suggesting a variation of the mechanism as compared with low fluence irradiation. The polymer is only partly ablated and the remaining crosslinked polymer can be decomposed to carbon species, especially with the higher photon energy of the 248 nm laser.

In the case of 308 nm irradiation first some microstructures are created, but the ablated surface becomes smooth again after additional pulses. The chemical composition also remains unchanged after several pulses, shown by the constant contact angles and atomic ratios (Fig. 7). This suggests a photochemical mechanism, removing the polymer completely layer by layer without any re-deposition of ablation products.

To test whether a photochemical mechanism alone can be used to explain the above described behavior for 248 and 308 nm irradiation, we applied a model developed by Pettit et al.¹⁴ for a photochemical mechanism.

3. Laser transmission and modeling

This model assumes a first and second excited state with the corresponding absorption crosssections σ_1 and σ_2 . In equation 1 and 2 the single photon absorption for ablation depth and transmission ratio is described,

$$d = \frac{1}{\rho} (S_0 - S_{th}) + \frac{1}{\rho \sigma_1} \ln \left(\frac{1 - e^{-\sigma_1 S_0}}{1 - e^{-\sigma_1 S_{th}}} \right) \quad (1)$$

where d = the etch rate, S_0 = photon density striking the surface target, S_{th} = photon density at the threshold fluence, ρ = chromophore density, and σ = absorption cross-section.

$$\frac{T_H}{T_L} = \frac{e^{(\rho \sigma_1 d)}}{\sigma_1 S_0} \ln \left(1 + \frac{e^{(\sigma_1 S_0)} - 1}{e^{(\rho \sigma_1 d)}} \right) \quad (2)$$

where T_H = transmission of the laser pulse at various fluences and T_L = transmission of the sample measured with low energy, e.g. a UV-Vis spectrometer.

The model can be extended to two-levels of excited states (scheme 1), as described in equation 3

$$\frac{dS}{dx} = -\rho \sigma_2 S - \rho \frac{\sigma_1 - \sigma_2}{\sigma_1} \left[1 - e^{(-\sigma_1 S)} \right] \quad (3)$$

where S = photon density in the laser pulse (F/h), x = depth in the target, σ_1 = absorption cross-section of the first excited state and σ_2 = absorption cross-section of the second excited state. The absorption cross-sections can be calculated according to (4),

$$\alpha_{lin} = \rho * \sigma \quad (4)$$

where ρ = chromophore density and σ = absorption cross-section.

The chromophore density can be calculated according to (5)

$$\rho = n * \rho_m \quad (5)$$

where ρ = chromophore density, n = number of chromophores and ρ_m = the monomer density. The maximum theoretical change of the transmission ratio can be calculated according to (6)

Fig. 8: Ablation depth vs. pulse fluence relationship for the 308 nm XeCl excimer laser irradiation of a 200 μm thick polymer film. The dash-dot curve indicates the predicted relationship based on Beer's law. The continuous curve uses $n = 4$ to reach a satisfying fit. The dash curve shows the result of different fit parameter, $n = 12$, which must be used to reach a satisfying fit of the transmission ratio in Fig. 9.

$$\left. \frac{T_H}{T_L} \right|_{\max} = \frac{1}{e^{-\alpha_{\ln} d}} = e^{\alpha_{\ln} d}$$

(6)

Fig. 9: Transmission ratio (high fluence transmission / low fluence transmission) vs. laser fluence at 308 nm. The discrete data points indicate the experimental results. The linear behavior is indicated with the line at $T_H/T_L = 1$, whereas the line at $T_H/T_L = 5.26$ indicates the theoretical maximum value for the transmission ratio according to (6). The solid curve is the result of applying the fit parameter of Fig. 8, which gives a satisfying result for the ablation rate a satisfying result. The dashed line shows the result of a fit which gives better results for T_H/T_L .

We measured the transmission of the laser pulse and applied the model, described by equations 1-6 to our data, as shown for the case of 308 nm irradiation, in Fig. 8 and 9. For both data sets, etch rate and transmission ratio T_H/T_L , the two-level model must be applied. With this model, it was possible to obtain a good fit of the ablation rate up to a fluence of about 20 J cm^{-2} as shown in Fig. 8, for the polymers films with a thickness of about 200 μm . For this fit, values for $\rho = 7.60 \cdot 10^{21} \text{ cm}^{-3}$, $\sigma_1 = 2.184 \cdot 10^{-17} \text{ cm}^2$, $\sigma_2 = 1.420 \cdot 10^{-19} \text{ cm}^2$ were used which correspond to a chromophore number (n) of 4. These values are consistent with the values discussed previously. The result of this fit is shown as the solid curve in Fig. 8, where the etch rate based on Beer's law is also included. This line is obviously much lower than the experimental values. Unfortunately, it was not possible to use the same set of fitting parameters for the transmission ratio. The fit with $n = 4$, shown in Fig. 9 by the solid line, increases much earlier (close to 10 mJ cm^{-2}) than the measured values, and nearly reaches the theoretical maximum value.

For 248 nm irradiation we also applied the two level model. We could achieve satisfying fits for both data sets (etch depth and transmission ratio), but due to the limited set of experimental data, no decisive conclusion could be drawn. In the case of 308 nm irradiation it seems to be necessary to add additional parameters to the model, e.g. decomposition energy of the polymer or other thermal parameters.

To address the issue of a possible photothermal contribution we applied ns-photography and ns-surface interferometry.

4. ns-Photography and ns-interferometry

A nanosecond imaging technique¹⁰ which produced a series of shadowgraphs at the air-polymer interface region has been employed to study laser ablation plumes from a triazene polymer after various time intervals. This produced a series of shadowgraphs which were recorded with a CCD camera for two series of experiments using laser fluences of 250 mJ cm^{-2} and 50 mJ cm^{-2} . Although the photos taken just before the peak of the excimer laser are well after, approximately 25 ns, the beginning of the pulse, they do not indicate any material ejection. However, those taken after the peak indicate a rapidly ejected plume which forms a blast wave in the air in front of it. In the photos taken at times less than 100 ns after the peak pulse only one front can be observed in both fluence cases but, for those after 100 ns two separate fronts are observed. An

example photo of the plume and blast wave fronts photographed is shown in Fig. 10 for the 250 mJ cm⁻² case 204 ns, 407 ns and 1000 ns after the peak pulse. The photos also confirm the total absence of solid products, as suggested from the lack or re-deposited material after irradiation (Fig. 1).

Fig. 10: Photos, showing the shock frons formed after irradiation with 250 mJ cm⁻². Left: 204 ns; middle : 407 ns; right: 1000 ns.

The average velocity of the initial single front and then the plume and blast wave was calculated between sets of sequential photos based on the center distance from the initial polymer surface and the time elapsed between the photos. These average velocities show that the initial single front velocity rapidly decays to well below both the initial product front and blast wave velocities. After this, the product front and blast wave appear, and their velocities decay smoothly. The erratic behavior of the initial front velocity may indicate instability in the chemical reaction or a change in the ablation mechanism during the first 100 ns. This is supported by separate ablation depth vs. time measurements (Fig. 12) which show that the ablation begins around the excimer laser peak and continues for approximately 75 ns.

The two balst wave structure, photographed in these experiments, has previously been compared to a micro-explosion. Point blast wave equations which neglect the explosive, or in this case, the ablated polymer mass have been shown to fit the blast wave propagation radius vs. time data¹⁵. However, the observ d blast waves in this investigation are within an order of magnitude of the minimum propagation radius, $R_{min}=[3M_0/2\pi\rho_0]^{1/3}$, so the ablated polymer mass must be included in the analysis^{15b}.

Two analytical solutions for the blast wave propagation distance, R , vs. time, t , are readily available; one for a planar geometry¹⁶, i.e. shock tubes, and the second for spherical or hemispherical geometry¹⁷. Both solutions assume instantaneous transfer of the "explosive" energy, E_0 , to the product gases and uniform distribution of the compressed air and product gases behind their respective shocks. In the planar case, one-dimensional hydrodynamic conservation laws along with the above assumptions give¹⁶

$$R=\{[1.5C_1E_0^{1/5}t+C_2^{3/2}]^{2/3}-C_2\}/C_1 \quad (7)$$

$$\text{where} \quad C_1=\rho_0A[1/(\gamma-1)+4/(\gamma+1)]/(\gamma+1) \quad \text{and} \quad C_2=A\rho_sd[2/(\gamma+1)]^2/8$$

Here γ is the specific heat ratio of air (1.4), A is the planar area ablated (2.021 mm²), ρ_s is the solid polymer density (1.2 g cm⁻³), ρ_0 is the air density (1.184x10⁻³ g cm⁻³) and d is the ablation depth (50 nm in the 50 mJ cm⁻² and 650 nm in the 250 mJ cm⁻² fluence case). The hemispherical solution is in the form of a derivative¹⁷,

$$dR/dt=[E_0/(C_3+C_4R^3)]^{1/2} \quad (8)$$

$$\text{where} \quad C_3=4\pi\rho_sR_s^3/[3(\gamma+1)^2] \quad \text{and} \quad C_4=4\pi\rho_0[2/(\gamma+1)^2+1/(\gamma^2-1)]/3$$

Here R_s is the radius of a hemispherical piece of solid polymer with equal volume to that ablated. A simple fourth-order Runge-Kutta solution method is applied to solve the derivative for propagation radius.

For both the planar and hemispherical solutions, the explosive energy was replaced with either just the full laser irradiation energy^{15a-d}, $E_0 = E_{ls}$ (1.011 mJ for the 50 mJ cm⁻² and 5.053 mJ for the 250 mJ cm⁻² fluence case), or the sum of the full laser irradiation energy and the decomposition enthalpy^{15e}, $H_{th} = -623.5 \text{ J g}^{-1}$, of the ablated polymer, $E_0 = E_{ls} + H_{th}$ ($H_{th} = 0.076 \text{ mJ}$ for the 50 mJ cm⁻² and 0.983 mJ for the 250 mJ cm⁻² fluence case). Due to the absorptivity of the polymer, 4.56 mm⁻¹ for a 351 nm excimer laser, only 5.1% and 99.8% of the laser irradiation energy should be absorbed in the ablated depth for the 50 mJ cm⁻² and 250 mJ cm⁻² fluence cases, respectively. However, a parametric study showed that 100% absorption was necessary for the models to come close to matching the data. This 100% absorption is possible since the absorptivity is

measured below the ablation threshold and the products or non-linear absorbance changes may result in the absorption a large portion of the irradiated energy.

A comparison of both fluence cases using both the planar and hemispherical solutions shows that the best fit to the blast wave propagation distance as a function of time is obtained using the planar model with the full laser irradiation energy and decomposition enthalpy used as the "explosive energy," as is shown in Figure 11 for the 250 mJ cm^{-2} fluence case. Given that the ablated area is approximately a $1.63 \times 1.24 \text{ mm}$ square, the planar case is expected to initially apply until the edge effects come into the center after which the hemispherical case should apply; however, the planar case seems to give the best results for the complete time measured.

The two plume structure of the ablation products suggest that there are either two separate sequential or independent chemical reactions or the same unstable reaction of the polymer that initiates and quenches and then again re-initiates. The application of the model for a microexplosion in the case of laser ablation shows the influence of additional (not laser) energy sources, e.g. explosive energy, which could explain the failure of the pure photochemical model.

It has been shown previously, that ns-interferometry has the potential to distinguish between photochemical and photothermal mechanisms¹¹: a photothermal mechanism results in the pronounced swelling of the polymer surface and a delayed material ejection. The surface interference fringes were imaged after various time intervals for fluences of 60 mJ cm^{-2} and 250 mJ cm^{-2} . Example images are shown in Fig. 11 with time intervals of 8 and 58 ns after irradiation with 250 mJ cm^{-2} . The analyzed data are shown in Fig. 13 for irradiation with 250 mJ cm^{-2} . Etching of the film starts and ends during the laser pulse (shown in Fig. 13), suggesting a predominant photochemical mechanism. A closer inspection of the initial stages of ablation, or at lower fluences, reveals a modified behavior. The film initially swells slightly, followed by immediate etching. This indicates a photothermal part of the ablation which is less pronounced at higher fluences.

Conclusion

The existing data show that laser ablation can be used as a "true" high resolution dry etching technique, if tailored polymers are used. The combination of photolabile energetic groups in the polymer main chain, which decompose to gaseous products, results in clean etching contours with no surface contamination by ablation products. The specially designed triazenopolymers reveal some unique features: wavelength selective surface modification and etching. The data analysis also shows that the mechanism is mainly dominated by photochemical features (clean etching, no surface modification, etching starts and ends with the laser pulse), but that additional parameters, such as the decomposition energy also influence the mechanism. The amount of these additional parameters varies with the applied laser fluence, suggesting a non-linear pump dependence of the ablation process.

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