



Laser induced chemical and physical modifications of polymer films: dependence on the irradiation wavelength

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Abstract

Polymers with photolabile groups absorbing in the mid UV (around 300 nm) were irradiated with excimer-lasers (248 and 308 nm). Irradiation with 248 nm (KrF laser) corresponds to an excitation of the photostable phenyl system whereas the XeCl laser (308 nm) excites the labile triazeno groups ($-N=N-N<$). Thin polymer films (0.1–3 μm) were coated onto quartz or glass and irradiated below and above the threshold of ablation. The films were subsequently analyzed with various surface analysis techniques. Below the threshold of ablation the main feature at both irradiation wavelengths was the reduction of the absorption maximum at about 330 nm and an increase of the surface oxygen content (X-ray photoelectron spectroscopy) and therefore the surface polarity (contact angle). The surface remained smooth with no detectable micro-structures (scanning electron microscopy). Above the ablation threshold the absorbance at 330 nm decreased dramatically and the color of the film changed. For 248 nm irradiation the surface was darkened and a carbonization (XPS) with microstructures (SEM) was detected. The surface became non-polar in agreement with surface carbonization. In the case of 308 nm irradiation the surface remained smooth and no change of the chemical composition or surface polarity was detected, suggesting a photochemically induced layer by layer ablation process.

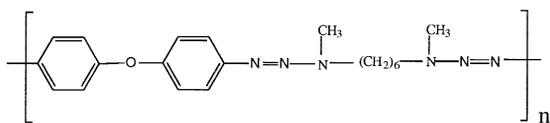
1. Introduction

The use of lasers in polymer science has become a vast field of interest [1]. Lasers are used as analytical tools and for many applications like material processing and information storage. Material processing applications have become available with the advent of high energy pulsed lasers. Excimer lasers are particularly interesting for structuring of polymers in a one step dry etching process [2]. This application is closely related to ablation of polymers,

a process first reported in 1982 [3]. Since the first reports, numerous studies have been published, but there is still no generally accepted mechanism of polymer ablation. The different suggestions are thermal, photothermal, photochemical mechanisms and/or a mixture of these [4–6].

In most studies of polymer ablation standard polymers were used. A different approach to use laser ablation for dry etching applications was the development of polymers designed for ablation [7]. These polymers consist of a photolabile $-N=N-N<$ (triazeno) group in the main chain of the polymer and have an absorption maximum around 300 nm. Pronounced differences in the maximum etch rates [8]

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Scheme 1. Structural unit of the triazenopolymer.

and transmission behavior [9,10] between 248 nm and 308 nm irradiation have been detected, suggesting variations in the acting mechanism.

In this study, surface analytical techniques were used to study one selected polymer (Scheme 1) after laser irradiation with 248 and 308 nm to get more information about the acting mechanism. This specific polymer has been chosen because 248 nm corresponds to an absorption minimum ($\alpha_{248} = 66000 \text{ cm}^{-1}$) whereas 308 nm is close to an absorption maximum ($\alpha_{308} = 166000 \text{ cm}^{-1}$).

2. Experimental section

The polymer was synthesized according to a procedure described elsewhere [11]. Thin films of variable thickness were prepared using the solvent cast technique with spectroscopic grade solvent (chloroform, Aldrich). As substrate, either glass or quartz wafers were used. Irradiation of the polymer films was carried out using a Lambda Physik EMG 102 MSC excimer laser at 308 nm and a Lambda Physik EMG 201 MSC excimer laser at 248 nm. The energy was measured with a Gen-Tec joule meter, model ED 500. The scanning electron microscopy (SEM) pictures were taken on a Topcon DS 720 instrument. X-ray photoelectron spectroscopy (XPS) were measured with a Perkin Elmer Phi 5600 instrument.

3. Results and discussion

3.1. SEM

SEM pictures were taken after irradiation at both wavelengths with fluences below and above the threshold of ablation after various numbers of pulses.

After irradiation at both wavelengths with fluences below the threshold of ablation *no* changes of the surface morphology could be detected. The sur-

face appears still very smooth indicating that the changes observed in the contact angle measurements (discussed below) are due to chemical surface changes.

A totally different behavior was observed for the higher energies. After 308 nm irradiation with 30 mJ cm^{-2} a roughening of the surface was detected. The microstructures reached a maximum intensity after about 10 pulses and got weaker with successive pulses.

In the case of the 248 nm irradiation the surface appeared different. A well pronounced 'nap' structure is detected with growing nap sizes to reach, after 250 pulses, a size of about $5 \mu\text{m}$. On the top of the naps additional material is detected, which grow in some cases to 'tree like' structures (shown in Fig. 1). It can also be seen that this material did not cover the surface completely.

3.2. Contact angle

To study whether chemical modifications take place, in addition to the physical changes of the surface, contact angle measurements were used.

For the fluences below the threshold of ablation a similar behavior for both irradiation wavelengths was observed. The contact angle decreased from 57.5° to about 20° . The SEM pictures showed that no surface roughening took place which could cause a decrease of the contact angle [12]. Therefore the change of the contact angle is due to chemical alterations of the surface. The polarity of the surface

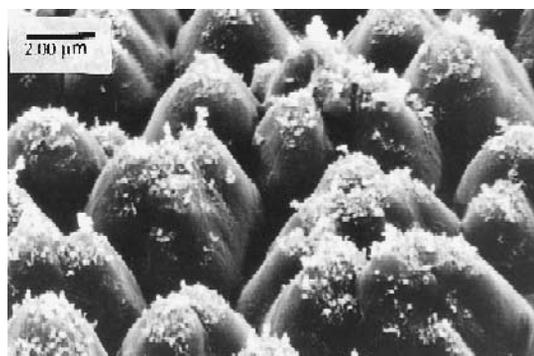


Fig. 1. Scanning electron micrographs of surface changes after 250 pulses with 36 mJ cm^{-2} at 248 nm, with a magnification of 5000.

increased, caused by reaction of radical sites at the surface with atmospheric oxygen or moisture. The radicals are thought to be the product of the pathway of photo decomposition.

In the case of irradiation fluences above the threshold of ablation different behaviors are observed. For 308 nm irradiation the contact angle decreased slightly. This is in agreement with the SEM pictures which show a slight roughening of the surface. With 248 nm irradiation a more complex behavior is observed. First the contact angle decreases, due to the observed growing of the microstructures. After more than 5 pulses the trend changes and the contact angle increases drastically although the SEM pictures show the development of more pronounced microstructures. Therefore a large change of the surface polarity must be the reason for this behavior. For more than 60 pulses the surface appears black and the contact angle becomes time dependent. If the contact angle is measured immediately after the irradiation, values of about 80° result, but also fast darkening of the water droplet and decreasing angle is observed. If the contact angle is measured after 24 h or more the values are constant at about 140° and the water droplet does not turn black. The value indicates a very nonpolar surface like carbon or graphite, which would also explain the black color.

3.3. XPS

In order to get more information about the chemical changes of the polymer surface, high vacuum surface spectroscopic techniques were used. The relative changes in percent of the O/N, O/C and N/C atomic ratios, relative to the untreated polymer, were used to analyze the surface modifications after laser treatment. The untreated polymer corresponds to the 100% data points in the Figs. 2–4.

The irradiation with fluences below the threshold of ablation revealed for both irradiation wavelengths a similar behavior. In the case of 248 nm irradiation (Fig. 2) an increase of O/N and O/C is detected, whereas the N/C ratio decreases. The main changes of the ratio take place during the first 250 pulses and stays then constant up to 2500 pulses. The increases of the two oxygen ratios show clearly that the surface has a higher O content than prior to irradiation.

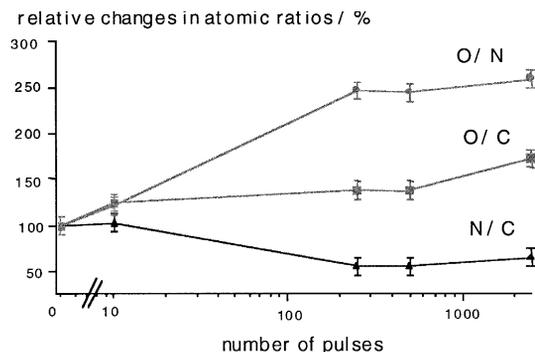


Fig. 2. Relative changes in atomic ratios in % of the triazenopolymer after irradiation with various pulse numbers with 9 mJ cm^{-2} at 248 nm. The untreated polymer = 100%.

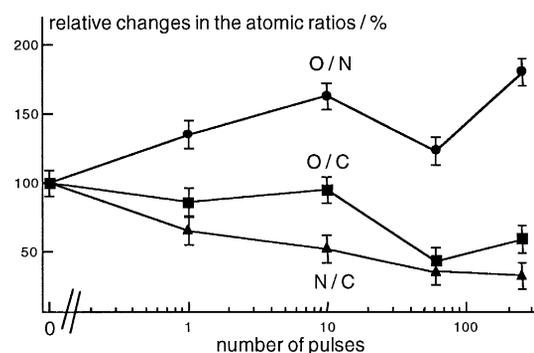


Fig. 3. Relative changes in atomic ratios in % of the triazenopolymer after irradiation with various pulse numbers with 36 mJ cm^{-2} at 248 nm. The untreated polymer = 100%.

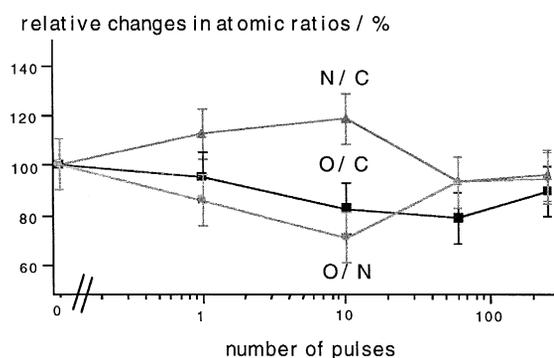


Fig. 4. Relative changes in atomic ratios in % of the triazenopolymer after irradiation with various pulse numbers with 30 mJ cm^{-2} at 308 nm. The untreated polymer = 100%.

It has also been determined that the N-functionalities are preferentially removed. In the case of the 308 nm irradiation the same kind of changes of the ratios are found. The main feature for irradiation with laser fluences below the threshold of ablation is the surface oxidation and preferential loss of nitrogen. Both are in line with photolytic decomposition of the N–N bond, creating an unstable $-N=N'$ radical, which decomposes on a very fast time scale [13]. Nitrogen is released and the radicals react with atmospheric oxygen or moisture to increase the surface oxygen content and therefore the polarity of the surface.

For irradiation with fluences above the threshold of ablation a totally different behavior is detected. For 248 nm (KrF laser) irradiation only the O/N increases, whereas the O/C and N/C ratios decrease (Fig. 3). Particularly the decrease of the O/C ratio shows that no surface oxidation take place but rather a carbonization. The two other ratios indicate again the release of nitrogen. This is in agreement with the non-polar surface measured with the contact angle and the black appearance of the polymer films after irradiation. A broadening of the XPS peaks after irradiation and non-soluble residues after irradiation suggest that crosslinking takes place in the bulk of the polymer. The higher penetration depth of the laser at 248 nm and the higher photon energy can result, in crosslinking of the polymer, followed by a decomposition of the polymer-network resulting in carbon species.

In the case of 308 nm irradiation with fluences above the threshold of ablation, the most complex behavior is found (Fig. 4). Only minor changes took place between 1 and 10 pulses. These changes can be attributed to removal of oxygen and carbon surface contaminations and also correspond to the largest roughening of the surface, which can also influence the relative atomic ratios. After 10 pulses the atomic ratios reach, within the error of the experiment, the starting values again. This indicates that no surface modification takes place and the polymer is ablated layer by layer.

4. Conclusion

Surface analysis techniques have been used to demonstrate that the polymer surface is modified

selectively with different laser irradiation wavelengths. The two laser energy ranges, 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 surface oxidation, as shown with the contact angle and XPS measurements. The oxidation is a result of the radical pathway of photo decomposition of the triazeno chromophore.

At fluences above the threshold of ablation for each wavelength a different behavior is observed. After irradiation with 248 nm growing 'nap' like structures are detected. The surface appeared black and carbonized, suggesting a thermal or different photochemical mechanism, caused by the higher penetration ($\alpha_{308} = 166000 \text{ cm}^{-1}$, $\alpha_{248} = 66000 \text{ cm}^{-1}$) depth of the laser. The radicals created in the polymer bulk can lead to crosslinking of the polymer, which results in a volume contraction of the polymer. This is also a possible mechanism for the formation of the observed microstructures. Upon further irradiation the crosslinked polymer is decomposed to carbon species. In the case of 308 nm irradiation the ablated surface becomes again smooth after some initial roughening. The chemical composition remained unchanged after several pulses, suggesting a photochemical mechanism, removing the polymer layer by layer without any redeposition of ablation products.

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