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Applied Surface Science 197–198 (2002) 786–790

applied
surface science

www.elsevier.com/locate/apsusc

Incubation and ablation behavior of poly(dimethylsiloxane) for 266 nm irradiation

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Abstract

Poly(dimethylsiloxane) (PDMS) has been irradiated with a frequency quadrupled Nd:YAG laser (266 nm) at a repetition rate of 1 Hz. The analysis of etch depth vs. pulse number data reveals a pronounced incubation behavior, i.e. ablation starts only after several pulses. The threshold of ablation (210 mJ cm^{-2}) and the corresponding effective absorption coefficient ($\alpha_{\text{eff}} = 48900 \text{ cm}^{-1}$), which is very different from the linear absorption coefficient (nearly zero), were determined. Incubation of polymers during ablation is normally related to changes of the chemical structure of the polymer. The incubation behavior of PDMS upon 266 nm irradiation was studied with UV-Vis spectroscopy, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, X-ray photoelectron spectroscopy (XPS) and Raman microscopy. The experimental data obtained with these techniques suggest that upon incubation O–H and Si–O groups are formed along with an increase in surface roughness. Ablation starts as soon as the absorption reaches a certain threshold. The ablation products consist of a silica-like material and carbon in the form of soot with some crystalline features.

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Keywords: Ablation; Incubation; IR spectroscopy; Laser; Poly(dimethylsiloxane); UV spectroscopy

1. Introduction

Poly(dimethylsiloxane) (PDMS) is an important technical polymer, and the modification of the surface is a growing research field. One possible approach for modifying the surface is the application of UV irradiation. Surface modification can result in the conversion of the polymer surface from hydrophobic to hydrophilic without etching or physical structuring. The surface modification of PDMS by ultraviolet radiation in the presence of atmospheric oxygen [1] or by

plasmas generated by partial corona discharge [2] was reported previously. However, these techniques do not allow a structuring of the surface without using a mask. In spite of the low linear absorption coefficient (nearly zero) of PDMS (Fig. 1) at 266 nm, it is possible to structure PDMS with fluences $> 210 \text{ mJ cm}^{-2}$. This behavior is ascribed to incubation [3] where chemical surface modifications occur without altering the bulk properties of the polymer [4].

2. Experimental

Films of cross-linked PDMS have been prepared by evaporating a 12 wt.% solution of vinyl-functionalized

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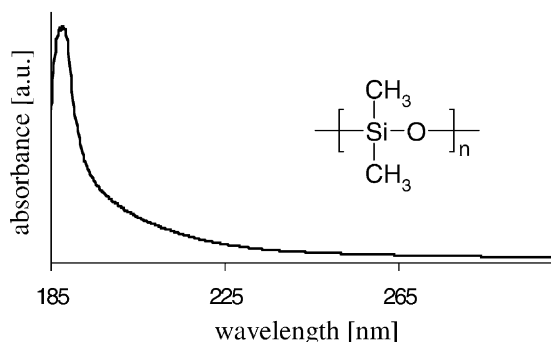


Fig. 1. UV absorption spectra of PDMS in the range 185–300 nm.

PDMS, poly(methylsiloxane) as a cross-linker and a Kartstedt platinum catalyst in isooctane in polystyrene Petri dishes. The films are cured for 5 min at 100 °C after evaporation of the solvent. For UV-Vis measurements, quartz (Suprasil I) substrates have been used. The resulting film thickness (average of about 250 μm) was measured by a profilometer (Dektak 8000).

As irradiation source, a frequency-quadrupled ($\lambda = 266$ nm) Nd:YAG laser (Quantel Brilliant B, 1 Hz, $\tau = 6$ ns) was used. The laser beam was focused with a spherical lens ($f = 400$ mm) onto the sample surface. The etch depth of the irradiated area was determined by the profilometer.

Diffuse reflectance infrared Fourier transform (DRIFT) IR spectroscopy measurements were performed using a Bruker 55s FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. All samples were analyzed in a diffuse reflectance unit (Specac). The samples were prepared by filling the powder sample holder with a thin layer of SiC powder (400 meshes). Then the background spectrum (256 scans, resolution 2 cm⁻¹) was measured and five drops of the 12 wt.% solution of PDMS were added. After evaporation of the solvent, the samples were allowed to cure for 5 min at 100 °C. UV spectra were recorded with a Varian Cary 500 UV-Vis spectrometer. Raman spectra were measured with a Raman microscope (Labram, DILOR) equipped with an objective (100× magnification) and a thermoelectrically cooled charge-coupled detector. Spectra were acquired between 250 and 2000 cm⁻¹ with a Kr⁺ ion laser operating at 530.9 nm with a laser power of ≈ 1 mW. The X-ray photoelectron spectroscopy (XPS) spectra were recorded with an ESCALAB 220I XL (VG

Scientific) photoelectron spectrometer, using Mg K α radiation at a source power of 100 W.

3. Results and discussion

PDMS was irradiated at 266 nm at various fluences and pulse numbers. The plots of etch depth vs. pulse number at a given fluence clearly reveal that incubation takes place. Etching starts only after several pulses (Fig. 2). The obtained etch rates were plotted vs. the logarithm of fluence (Fig. 3). The following equation [5] was used to calculate the threshold fluence (F_0) and the effective absorption coefficient (α_{eff}) where $d(F)$ is the etch rate at a given fluence F :

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

An ablation threshold fluence $F_0 = 210 \pm 60$ mJ cm⁻² and an effective absorption coefficient $\alpha_{\text{eff}} = 48\,900 \pm 2800$ cm⁻¹ were derived. The effective absorption coefficient is very different to the linear absorption coefficient (nearly zero). The incubation behavior is closely related to an increase of absorption during irradiation with the first laser pulses.

The increase of absorption at 266 nm was quantified by UV-Vis spectroscopy. The changes of the UV absorption (at 266 nm) of PDMS are shown in Fig. 4 for various fluences. After irradiation, an overall increase of the absorption without any spectral features was detected in the range 500–185 nm. At higher

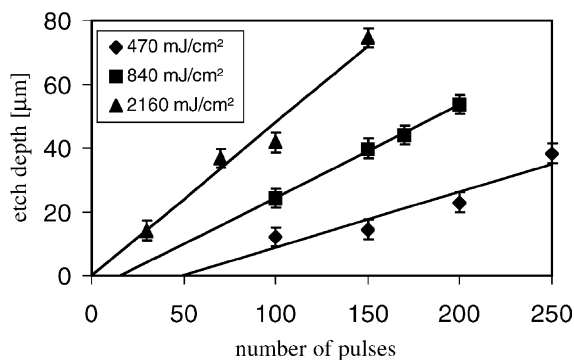


Fig. 2. Plot of etch depth vs. number of pulses for three different fluences; at 470 mJ cm⁻² ablation starts after 49 pulses, at 840 mJ cm⁻² ablation starts after 16 pulses and at 2160 mJ cm⁻² ablation starts right with the first pulse.

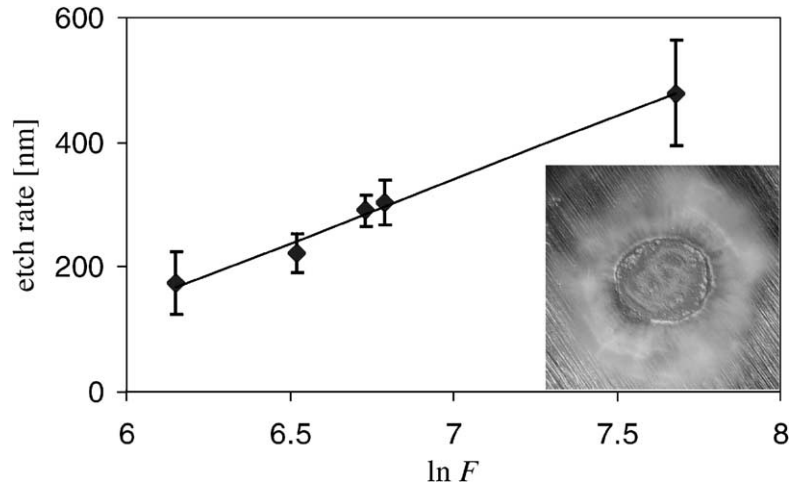


Fig. 3. Plot of etch depth/pulse vs. $\ln F$. Inset: photograph of the irradiated area of PDMS. A 'white ring' is formed by the ablation products.

fluences (or pulse numbers), an ablation crater is formed (inset in Fig. 3). A 'white ring' consisting of ablation products is clearly visible. Below F_0 no incubation/ablation behavior could be detected, whereas above F_0 a pronounced increase of the absorption was observed. This can be attributed to incubation, ablation and an increase of roughness with incubation as well as with ablation (Fig. 4). When ablation becomes the dominant process, the slope of the curves are getting smaller until the absorption decreases. The increase of roughness interferes with a quantitative determination of the threshold fluence by UV-Vis spectroscopy.

The incubation of polymers is normally related to changes of the chemical composition of the polymer.

An effective method for detecting changes in the chemical structure is IR spectroscopy. DRIFT spectroscopy measurements of the irradiated area were performed (inset of Fig. 3). The reference spectrum (Fig. 5) of the cross-linked PDMS obtained with the SiC sampling method is in good agreement with previous published data [6]. The assignment of the absorption bands is included in Fig. 5. Experiments were performed with fluences below the threshold of ablation (160 mJ cm^{-2}) and above (310 , 640 and 810 mJ cm^{-2}) with various pulse numbers. It is not possible to obtain quantitative data from the spectra due to a slight shift of the baseline and an overall increase of the intensity of all absorption bands, most probably due to the increased surface roughness.

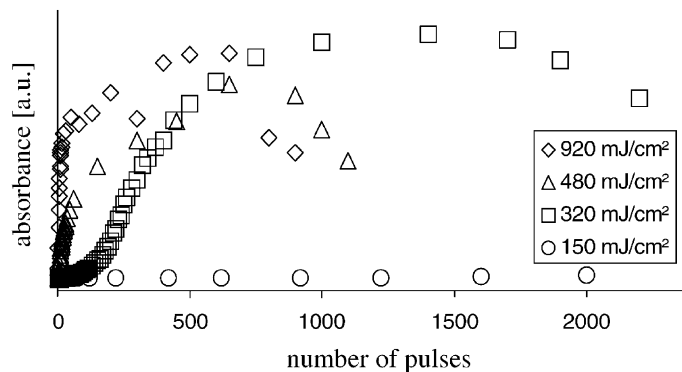


Fig. 4. UV absorption at a wavelength of 266 nm at four different fluences (ablation starts at 920 mJ cm^{-2} after about two pulses, at 480 mJ cm^{-2} after about 10 pulses, at 320 mJ cm^{-2} after about 65 pulses and 150 mJ cm^{-2}).

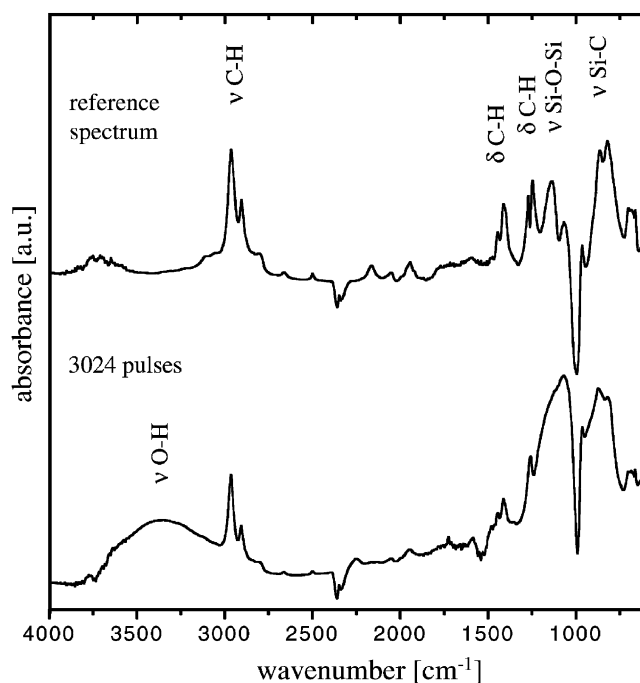


Fig. 5. DRIFT reference spectrum of PDMS obtained with the SiC sampling method. The following bands are assigned: $\nu(\text{C-H})$ at 2967 and 2960 cm^{-1} , $\delta(\text{C-H})$ at 1415, 1272 and 1251 cm^{-1} , $\nu(\text{Si-O-Si})$ at 1130 and 1065 cm^{-1} , $\nu(\text{Si-C})$ at about 860 cm^{-1} . A spectrum of the irradiated area of PDMS is included (fluence of 310 mJ cm^{-2} and 3024 pulses). The spectrum shows clearly the OH band at 3360 cm^{-1} .

Below the threshold of ablation (155 mJ cm^{-2}), an absorption band at 3360 cm^{-1} assigned to the hydroxyl group appears after about 280 pulses. This corresponds to an increase of the absorption band at 1130 cm^{-1} which is assigned to the Si-O-Si groups. A slight decrease is observed for the absorption bands corresponding to the stretching and deformation vibrations of C-H groups.

At higher fluences (319 mJ cm^{-2}) an overall increase of all bands is observed, followed by a pronounced increase (after ≈ 120 pulses) of the intensity of the absorption band at 1065 cm^{-1} (Si-O-Si groups). Simultaneously, a decrease of the bands assigned to C-H and Si-C groups can be observed. After about 200 pulses, an absorption band at 3360 cm^{-1} assigned to the vibrations of O-H groups can be identified. Upon further irradiation, the polymer decomposes and Si-O and O-H groups are formed without a complete removal of the decomposition products (>3000 pulses, Fig. 5). At even higher fluences (640 and 810 mJ cm^{-2}), all bands of the starting material decrease (after a certain delay)

and even the reaction products are removed after about 270 pulses.

XPS was applied to analyze the ablation products in the 'white ring' in more detail. The data in Table 1 show (compared to starting material) that the amount of carbon decreases, while Si (slightly) and O_2 (pronounced) increase. These data suggest that a silica-like material is created with an additional amount of carbon (30%). The presence of carbon was confirmed by Raman microscopy which is very sensitive for the detection of carbon (large Raman cross-section), but

Table 1
Quantitative elemental composition of the 'white ring' after irradiation with several pulses at a fluence of 450 mJ cm^{-2} (at.%) as determined by XPS

No. of pulses	C 1s	O 1s	Si 2p
0 (reference)	46	24	30
100	46	23	31
300	33	35	32
1500	35	34	31

quite insensitive to SiO_x (low Raman cross-section). The Raman spectra showed the typical D and G band of carbon [7], along with bands assigned to the native PDMS. This suggests that either incomplete coverage of the PDMS with carbon takes place or the layer of ablation products is quite thin. Combining the data obtained by XPS and Raman microscopy indicates that the ablation products consist of a silica-like material and a pronounced amount of carbon present in the form of soot with some crystalline features.

4. Summary

After irradiation of PDMS at 266 nm and analysis of the etch depth vs. pulse number data, a pronounced incubation behavior was observed. UV and IR spectroscopy studies confirmed an incubation process in which O–H and Si–O groups are generated with the first pulses. Additional Raman microscopy and XPS measurements were applied to analyze the ablation products. A silica-like material and polycrystalline graphitic carbon with a relatively high bond angle disorder were identified as the main solid ablation products.

Acknowledgements

Financial support of the Bundesministerium für Bildung und Forschung (BMBF) and the Swiss National Science Foundation is gratefully acknowledged.

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