

# Wettability and surface composition of poly(dimethylsiloxane) irradiated at 172 nm

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## INTRODUCTION

The Poly(dimethylsiloxane) (PDMS) is widely used in biomedical applications, membrane technology, microlithography as high voltage insulator [1] or in the crosslinked form as a nearly ideal elastomer. Its unique mechanical and optical properties, low weight, high durability, high gas permeability and excellent water repellency makes PDMS a widely used polymer [2, 3]. The modification of the hydrophobic PDMS to hydrophilic SiO<sub>x</sub> opens an additional wide range of applications such as its use in microelectronics [4 - 6], food packaging [7] and protective coatings for medical devices [8, 9].

The surface modification of PDMS to SiO<sub>x</sub> by ultraviolet radiation in the presence of atmospheric oxygen [10, 11] or by plasmas generated by partial corona discharge [12] was reported previously. The described processes employ restricted atmospheric conditions and rather long reaction times. Ambient conditions with shorter reaction times are more desirable. Photochemical modification of the PDMS surface by irradiation with lasers and excimer-lamps in the vacuum UV (VUV) region is a promising alternative.

In this report we describe the modification of PDMS at ambient conditions with a Xe<sub>2</sub>\*-excimer lamp emitting at 172 nm. The formation of active oxygen and ozone by the irradiation in air in combination with the irradiation itself causes a surface oxidation of PDMS to SiO<sub>2</sub>. The exposed surfaces were studied by contact angle measurements, diffuse reflectance Fourier transformed infrared (DRIFT) spectroscopy, X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry.

## EXPERIMENTAL

**Material.** Films of crosslinked PDMS were prepared by bar coating of a 12 wt% solution of vinyl-functionalized poly-(dimethylsiloxane), poly-(methylhydrosiloxane) as a cross linker and a Kartstedt platinum catalyst in isoctane on poly(ethylene terephthalate) plates. After evaporation of the solvent the films were cured for 5 minutes at 100°C, resulting in an average film thickness of about 8 μm.

For ellipsometry measurements the PDMS films were prepared by spin coating using the same solution (1 - 6.5 wt%) on silicon wafers. Spin-coated films were cured for 5 min at 100°C. In order to obtain different thicknesses the rotation speed (1500 and 2500 rpm) and/or the solution concentration was varied.

**UV-source.** Exposure to VUV light was performed with a water-cooled VUV excimer lamp of approximately 30 cm length mounted in a home-made assembly. The discharge was initiated in an annular gap between two coaxial quartz tubes containing xenon at 750 mbar emitting at a wavelength of 172 nm. The principles and properties of UV and VUV radiation generated by such excimer lamps were discussed elsewhere [13, 14]. The excimer VUV source was operated at frequencies of 225 to 280 kHz and a voltage amplitude of 10 kV. The PDMS films were irradiated at ambient conditions in air with intensities of 14, 32 and 50 mW/cm<sup>2</sup> at a constant distance of 2-5 mm to the VUV source.

**Analysis.** The wettability of the UV/ozone treated samples was studied using a G 2 contact angle goniometer (Krüss GmbH, Germany) using bidistilled water.

DRIFT spectroscopy measurements were performed using a Bruker 55s FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector and a diffuse reflectance unit (Specac). The samples were prepared by filling the powder sample holder with a thin layer of SiC powder (400 mesh). Then the background spectrum (256 scans, resolution 2 cm<sup>-1</sup>) was measured and 5 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 before recording the sample spectrum.

XPS were performed on an ESCALAB 220i XL instrument (Thermo VG Scientific). The photoelectron spectrometer was equipped with a magnesium X-ray source (hν = 1253.6 eV). In order to minimize the degradation of the PDMS films, the source was operated at a power of 100 W. Binding energies were normalized to the C 1s at 284.6 eV. The spectra were recorded in the constant analyzer energy mode with analyzer pass energies of 50 eV for the survey spectra and 20 eV for the high-resolution spectra.

Spectroscopic ellipsometry was performed using a spectroscopic ellipsometer (MOSS model ES 4G, Sopra, France) at an angle of incidence of 70°. The light source of the system was a Xe arc lamp (75 W). The energies were scanned from 1.5 - 4.5 eV at 0.05 eV intervals. The ellipsometer records tanΨ and cosΔ as a function of energy using Hadamard transformation of the reflected beam signal.

## RESULTS AND DISCUSSION

**Contact angle measurements.** The modification of the PDMS surface with irradiation by the Xe<sub>2</sub>\*-excimer lamp was first studied by wetting experiments. Figure 1 shows the static contact angles for water on the unirradiated and irradiated PDMS films at increasing irradiation times. The irradiated surfaces undergo a strictly linear decrease of the water contact angle with increasing irradiation time. The water contact angle of the unirradiated PDMS surface is 110° (hydrophobic) and decreases to 0° (hydrophilic, spreading). The change in the surface free energy is even more rapid when higher fluences were applied. At longer irradiation times no further changes of the contact angle was detected.

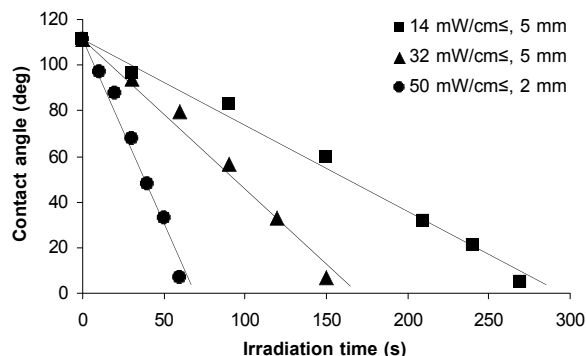
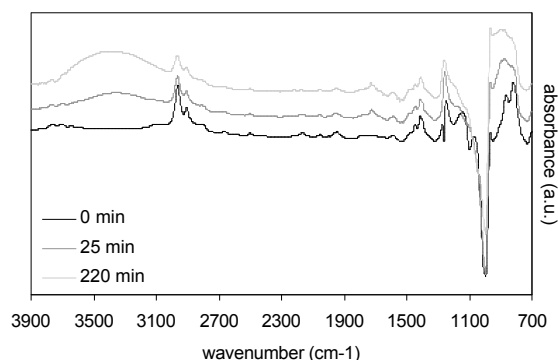


Figure 1. Static water contact angle on PDMS surfaces vs. irradiation time for various intensities. The lines are to guide the eyes.

**DRIFT.** The chemical changes in the surface composition of the irradiated polymer surfaces were studied by DRIFT spectroscopy. The reference spectrum is in accordance with previous published data (Figure 2) [15]. The symmetric and asymmetric stretching vibrations of the methyl groups can be found at 2967 and 2960 cm<sup>-1</sup>, the corresponding deformation vibrations modes are located at 1415, 1272 and 1251 cm<sup>-1</sup>. The asymmetric stretching vibrations of the Si-O-Si group appear between 960 and 1120 cm<sup>-1</sup>, the methyl rocking and Si-C stretching vibrations are centered around 797 cm<sup>-1</sup>. The measurement series plotted in Figure 2 is representative for irradiation experiments at intensities between 14 and 50 mW/cm<sup>2</sup>. Because of irregularities in the baseline an exact analysis of spectra below 1100 cm<sup>-1</sup> is not possible.



**Figure 1.** DRIFT spectra of native and irradiated PDMS (intensity 32 mW/cm<sup>2</sup>, 5 mm).

A decrease of all absorption bands characteristic for PDMS was observed, indicating a steady degradation of the polymer. The UV/air induced increase of the absorption band centered at 3300 cm<sup>-1</sup> is indicative for the formation of hydroxyl groups. From DRIFT alone we can not distinguish if only silanol groups (Si-OH) or/and Si-CH<sub>2</sub>OH groups are formed. However, according to our XPS data, the resolution of the C 1s peak indicates no presence of oxidized carbon atoms. This strongly suggests that the VUV irradiation at 172 nm results most likely exclusively in the formation of surface silanol groups.

**X-ray photoelectron spectroscopy (XPS).** XPS measurements indicate significant changes in the chemical composition of the PDMS upon irradiation. The XPS C 1s signal decreased drastically with increasing irradiation time. After 3 minutes the carbon content decreased from 47 at% (theoretical value for PDMS: 50 at%) to 17 at% and after 40 min to a final constant value of 4 at% (Table 1). (The difference is due to adventitious carbon, present on any sample exposed previously to air).

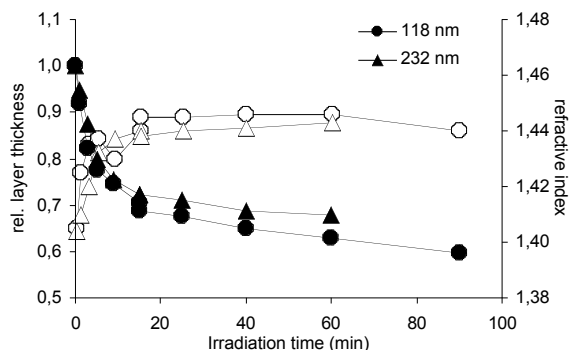
**Table 1. Atomic Concentration (at%) and O:Si Ratio Determined With XPS of Native and Irradiated PDMS (14 mW/cm<sup>2</sup>, 5 mm) Along With the Theoretical Values for PDMS.**

	C (at%)	O (at%)	Si (at%)	O:Si ratio
PDMS (theoretical)	50.0	25.0	25.0	1:1
PDMS (measured)	47.1	25.1	27.7	0.91 : 1
3 min irradiation	17.2	52.0	30.8	1.69 : 1
40 min irradiation	4.0	63.0	33.0	1.91 : 1

The atomic concentration ratio of O/Si starting at about 1 reaches values close to 2, which corresponds nicely to the composition of inorganic silicon dioxide (SiO<sub>2</sub>). This assumption was also confirmed by the binding energy shifts of the Si 2p and the O 1s levels, which shift to values characteristic for SiO<sub>2</sub>.

**Spectroscopic Ellipsometry.** Spectroscopic ellipsometry allows to measure the changes of the refractive index and the layer thickness induced by the UV-irradiation (Figure 3).

A rapid thickness decay can be observed for both films with ongoing irradiation. The curves fall more or less on each other. The corresponding values for n are 1.405 at 2.0 eV for untreated PDMS, which changes to 1.445 after 60 minutes of irradiation (Figure 3). This value is close to the literature value for SiO<sub>2</sub> of 1.457 [16]. Not only the electronic but also the optical properties of irradiated PDMS at ambient conditions is characteristic for inorganic SiO<sub>2</sub>.



**Figure 3.** Change of the relative layer thickness (●, ▲) and refractive index (○, △) vs. irradiation time of two PDMS films (initial total thicknesses: 118 and 232 nm, intensity 32 mW/cm<sup>2</sup>, 5 mm).

## CONCLUSION

Irradiation of PDMS at 172 nm at ambient conditions causes a rapid but controllable surface oxidation of the polymer. The formation of active oxygen and ozone by irradiation in air in combination with the irradiation itself leads to a formation of a close surface layer consisting of inorganic SiO<sub>2</sub>. A rapid but linear increase of the surface free energy due to the formation of surface silanol groups / SiO<sub>2</sub> was verified by means of contact angle measurements DRIFT, XPS and spectroscopic ellipsometry.

## ACKNOWLEDGEMENTS

Financial support of the Bundesministerium für Bildung und Forschung (BMBF) and the Swiss National Science Foundation are gratefully acknowledged. We thank Prof. I. Boyd and Dr. U. Kogelschatz for advice with the operation of the excimer lamp.

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