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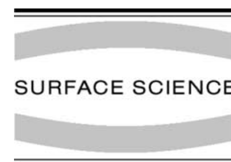

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UV-irradiation induced modification of PDMS films investigated by XPS and spectroscopic ellipsometry

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Abstract

UV-irradiation (172 nm) induced changes of PDMS surfaces were investigated with X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry (SE). Both methods indicate the modification of the PDMS to a silica-like surface (SiO_2). These conclusions could be drawn from the elemental composition determined by XPS and the binding energy shifts in the XPS spectra of the Si 2p and O 1s levels. Similarly the refractive index *n* determined with ellipsometry reaches a value close to the one of SiO_2. Additionally, ellipsometry allows to monitor the decrease of the original film thickness with increasing UV-irradiation time.

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1. Introduction

For many polymer applications the surface needs to be modified in order to improve its properties like wettability or adhesion. Consequently the modification of technically relevant polymers like poly-(dimethylsiloxane) (PDMS) is a growing research field. The surface modification of PDMS by ultraviolet radiation in the presence of atmospheric oxygen [1,2] or by plasmas generated by partial corona discharge [3] was reported previously. The described processes suffer from 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 eximer-lamps in the vacuum UV region is a promising alternative. The induced surface modification can result in the conversion of the polymer surface from hydrophobic to hydrophilic without ablation of the polymer. One possible application of modified PDMS films could be computer-to-plate driography, where anhydrous ink is used and no development steps are necessary.

In this work UV-irradiation induced modification of PDMS films by a Xe_2^* excimer lamp ($\lambda = 172$ nm) were investigated with X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry (SE). XPS provides information about chemical surface modifications, while

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thickness changes and changes in the refractive index *n* could be observed by SE.

2. Experimental

2.1. Film preparation

For the XPS measurements films of cross-linked PDMS were prepared by bar coating on poly-(ethylene terephthalate) plates (PET-plates) with a 12 wt% solution of vinyl-functionalized poly-(dimethylsiloxane), poly-(methylhydrosiloxane) as a cross-linker and a Kartstedt platinum catalyst in isooctane. After evaporation of the solvent the films were cured for 5 min at 100 °C, resulting in an average film thickness of about 8 μm.

For ellipsometry measurements films of cross-linked PDMS were prepared by spin-coating (1500 and 2500 rpm) with the same solution (1–6.5 wt%) on silicon wafers. After the spin-coating process the films were cured for 5 min at 100 °C. In order to obtain different thicknesses the rotation speed and/or the solution concentration was varied. The obtained films showed a sufficient adhesion to the substrate, which was tested with an adhesive tape.

2.2. UV-source

Exposure to short incoherent UV light was performed with a water-cooled UV excimer lamp of approximately 30 cm length (see Fig. 1), mounted in a Plexiglas box. 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. Tubes of Suprasil 1 quartz are chosen as dielectric barriers because of its dielectric properties and its superior UV transmission. The excimer UV source is driven at frequencies of 225–280 kHz and a voltage amplitude of 10 kV. The PDMS films were irradiated with intensity of approximately 30 mW/cm^2 in a distance of about 5 mm from the outer tube surface of the xenon excimer lamp.

2.3. X-ray photoelectron spectroscopy

XPS analyses of samples illuminated for different time periods were performed on an ESCALAB 220i XL instrument (Thermo VG Scientific).

The photoelectron spectrometer was equipped with a magnesium X-ray source ($h\nu = 1253.6$ eV). In order to reduce the degradation of the PDMS films, the source was operated at a power of 100 W. Binding energies were all referred to the C 1s at 284.6 eV. The spectra were recorded in the CAE mode (constant analyzer energy) with analyzer pass energies of 50 eV for the survey spectra and 20 eV for the high-resolution detail spectra.

2.4. Spectroscopic ellipsometry

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 xenon arc lamp (75 W). In our measurements the energies were scanned from 1.5 to 4.5 eV at 0.05 eV intervals. The

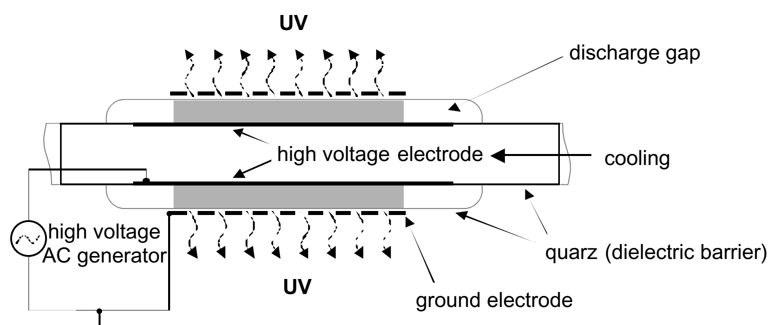

Fig. 1. Sketch of water-cooled Xe_2^* excimer lamp ($\lambda = 172$ nm).

ellipsometer records tan(Ψ) and cos(Δ) as a function of energy (wavelength) using the Hadamard transformation of the photo-detected signal.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

XPS measurements indicate large changes in the chemical composition of the irradiated PDMS even after a short irradiation time of a few minutes (see Table 1). The XPS C 1s signal decreases drastically with increasing UV-irradiation time. After 3 min the carbon content decreased from 47 at.%, which is close to the theoretical value of 50 at.% (see Table 1, inset in Fig. 4), to 17 at.%, to reach a final value of 4 at.% after 40 min of exposure. We have to consider that a part of this carbon signal is due to adventitious carbon, present on any XPS sample exposed previously to air. Additionally, the atomic concentration ratio of O/Si starting at about 1 reaches values close to two, which would correspond to a composition close to SiO_2. This fact is also confirmed by the shifts of the peak positions of the Si 2p and the O 1s levels, illustrated in Fig. 2 for the Si 2p level. The Si 2p binding energy for untreated PDMS is ~102.0 eV and shifts to 103.5 eV after 40 min of UV-light exposure. This peak position corresponds well to a measurement of SiO_2 quartz powder (see again Fig. 2) and literature values of 103.3–103.7 eV [4] for SiO_2. For the O 1s level the corresponding peak shifts from 532.3 eV for untreated PDMS to 533.2 eV after 40 min. The measured value corresponds again quite well with published data [4].

Table 1
Atomic concentration determined with XPS of untreated PDMS, and irradiated PDMS (3 min, 40 min) compared with the theoretical values for PDMS without considering the hydrogen, which cannot be detected by XPS

	C (at.%)	O (at.%)	Si (at.%)
PDMS (theoretical)	50.0	25.0	25.0
PDMS (measured)	47.1	25.1	27.7
Irradiated for 3 min	17.2	52.0	30.8
Irradiated for 40 min	4.0	63.0	33.0

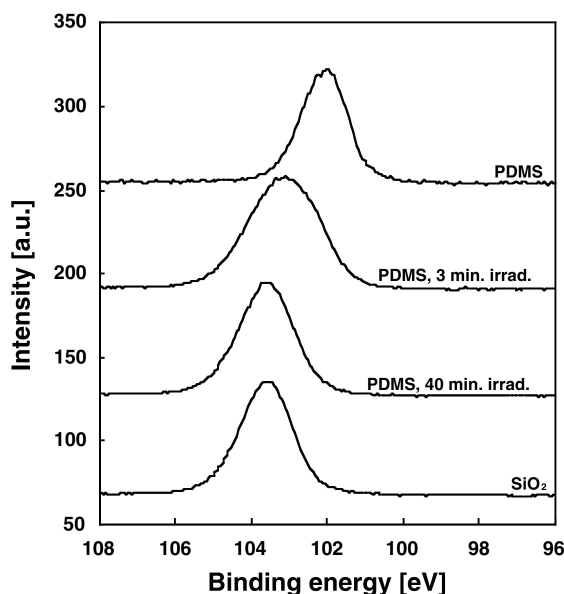

Fig. 2. Comparison of the XPS spectra of Si 2p level for a reference sample of SiO_2, as received PDMS films, and two irradiated PDMS films.

Additionally for short irradiation times a broadening of the Si 2p as well as for the O 1s peak is observed. For longer exposure times this effect disappears again. This broadening, corresponding to a shortening of the lifetime, could possibly be explained by a reduced crystallinity and/or conductivity [5] of the modified polymer surface. The presence of two intermediate species would also explain a broadening of the full width half maximum of the peak. In order to test this possibility the maximum entropy method [6] was applied. This method allows deconvoluting the intrinsic spectrum from the measured one. Rather small changes and shifts can be determined. The energy resolution can be enhanced typically by a factor of two. This method was applied successfully for a few investigations to resolve different species in a spectrum [7,8]. In our case no additional peak could be observed, what favors the explanation of the peak broadening by a reduced crystallinity and/or conductivity and not by the presence of two species.

In conclusion the XPS measurements show that the chemical composition and the electronic properties of the irradiated PDMS surface become

silica-like within the information depth of XPS (∼5–10 nm).

3.2. Spectroscopic ellipsometry

SE allows determining the optical properties of untreated and irradiated PDMS films. For transparent films ($k = 0$) it should be possible to determine the film thickness and the refractive index n simultaneously. With SE it is possible to monitor the changes of the refractive index and of the thickness induced by the UV-irradiation. The apparent thickness is the result of the analysis of the data with a single layer model. The native oxide layer (∼2 nm) on top of the silicon wafer was not included in the model.

Spin-coated PDMS films on silicon wafers were used for these measurements due to the higher surface quality of the substrate, resulting in a more homogeneous thickness of the PDMS films. Many films with different thicknesses were produced to check the reproducibility and to cover a rather wide thickness range (for spin-coated films). Fig. 3a shows the thickness changes of three different PDMS films irradiated with UV-light. The thickness decay has an exponential appearance for all three films. The three curves fall more or less on top of each other when the relative thickness change of these three films is plotted (see Fig. 3b). The corresponding values for n are 1.405 at 2.0 eV for untreated PDMS, increasing to 1.445 after 60 min of exposure (see Fig. 4). This value is close to the literature value for SiO_2 of 1.457 [9]. Similar to the electronic properties, the optical properties of irradiated PDMS become also silica-like. However, ellipsometry is probing the whole sample thickness and not only the surface regime like XPS.

At wavelengths below 190 nm oxygen molecules present in the surrounding atmosphere (air) can be easily dissociated due to a strong absorption band around 172 nm. The released oxygen atoms can subsequently form ozone, which can then be decomposed by further absorption of the VUV light [10], producing active oxygen species (radicals and excited molecular oxygen) reacting with the polymer surface. The surface and bulk modifications of PDMS films could originate from photons, heat,

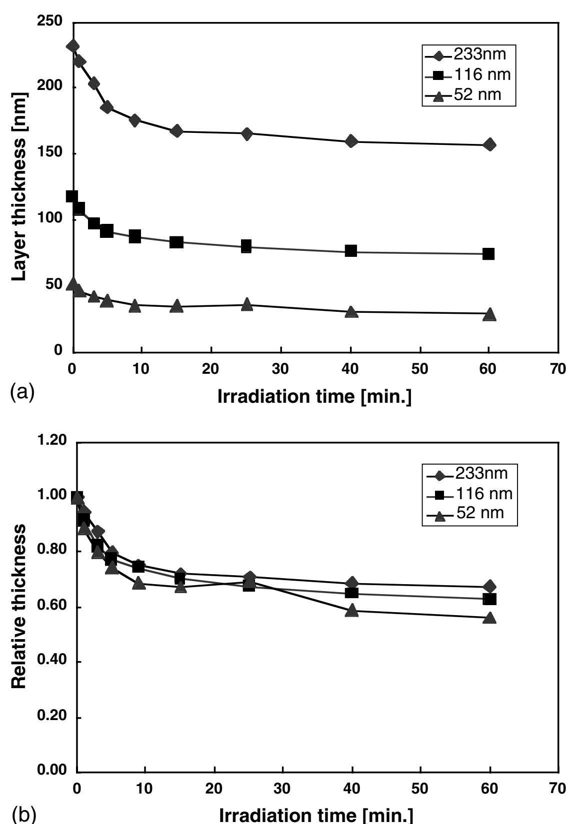

Fig. 3. (a) Film thickness determined with ellipsometry of three different PDMS films on silicon substrates vs. irradiation time. (b) Relative thickness changes determined with ellipsometry of three different PDMS films on silicon substrates vs. irradiation time.

ozone/active oxygen species, or various combinations. The fact that the relative thickness changes induced by the irradiation are the same for all films can only be explained by a mechanism, which takes place in the whole volume and not only at the surface. Active oxygen species would react mainly at the surface of the polymer and can thus be excluded. Ozone could probably diffuse into the polymer and influence the modification of the PDMS in the bulk material. Photons and heat can modify the material to the whole extent. The thermal load of the sample is reduced by the water-cooling of the excimer lamp and should therefore play only a minor role. Consequently, the photons would be the important parameter for the mechanism of surface modification of PDMS.

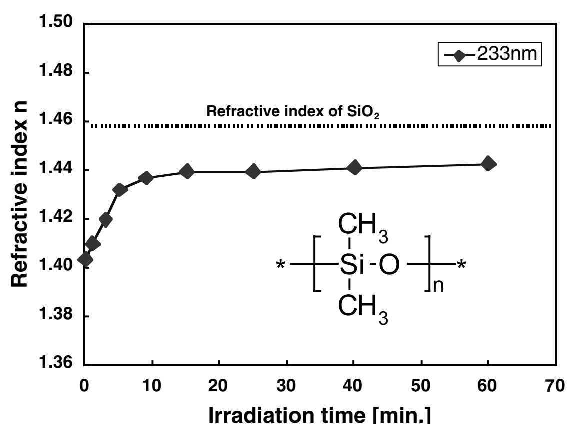

Fig. 4. Change of the refractive index n of a 233 nm thick PDMS films on silicon substrates vs. irradiation time. Inset: molecular structure of poly-(dimethylsiloxane) (PDMS).

As the overlap in Fig. 3b of the relative thickness changes is not complete and slightly higher thicknesses remain for thicker films, active oxygen species and/or ozone can also influence the surface modification to some extent. It would be very helpful to identify the volatile gas molecules (probably volatile oxidized carbon species), leaving the polymer, in order to describe the complete reaction mechanism. We will investigate this part of the reaction mechanism in further experiments in a vacuum chamber.

4. Conclusions

Due to the UV-irradiation the carbon content of the PDMS surface decreases with irradiation time indicated by the decrease of the XPS C 1s signal. Additionally the binding energies of the Si 2p and O 1s increase and reach the values corresponding to SiO_2. The atomic concentration ratio O/Si reaches also the corresponding value of two. SE revealed a decrease of the PDMS films thickness due to the UV-irradiation. The refractive index n increases with irradiation time, approaching the value of SiO_2.

Acknowledgements

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