

Neutron Reflectometry and Spectroscopic Ellipsometry Studies of Cross-Linked Poly(dimethylsiloxane) after Irradiation at 172 nm

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Poly(dimethylsiloxane) (PDMS) was irradiated under ambient conditions in air with a Xe₂*-excimer lamp. The formation of atomic oxygen and ozone during irradiation in air by V-UV photons results in the transformation of PDMS to silicon oxide. The irradiated surfaces were studied by spectroscopic ellipsometry and neutron reflectometry. The measurements revealed the formation of a rough, i.e., between 11 and 20 nm, oxidized surface layer and a decrease of the total layer thickness. The thickness of the oxidized layer decreased for a given PDMS thickness when the polymer was irradiated for longer times and/or higher intensities. The composition of the oxidized layer after irradiation was not uniform through the layer and consisted of a mixture of original polymer and silicon bonded to three or four oxygen atoms (SiO_x). The refractive index *n* determined by ellipsometry reaches a value similar to values reported for SiO₂.

Introduction

Poly(dimethylsiloxane) (PDMS) is an important technical polymer. The combination of organic and inorganic chemistry in one polymer gives rise to excellent material properties such as high thermal and oxidative stability, low toxicity, and good gas permeability. PDMS is physiologically inert and has excellent isolating and low adhesion properties.^{1–6} Since 1940, its further development led to utilization in resins, silicon oils, coatings, gums for advanced applications such as outdoor insulations, medical equipment, surgical replacements, and the printing industry.^{3,4,6–10} The hydrophobicity of PDMS provides a high surface resistivity and water repellence even in the presence of moisture and contaminants. The initially hydrophobic surface becomes progressively hydrophilic when treated with plasmas¹¹ and cold plasmas,^{12–14} irradiated with a low-pressure mercury-quartz lamp (185–

254 nm)¹⁵ or exposed to electric discharges¹⁶ or vacuum UV light emitted by an Xe₂*-excimer lamp.^{17–19} The hydrophilicity can be ascribed to the generation of hydroxyl groups, i.e., silanol groups, on the polymer surface. With proceeding irradiation time a silicon oxide layer is formed. However most of the described methods suffer from specific preparation methods, restrictive atmospheric conditions, high temperatures, and/or rather long reaction times. In terms of a future technological application, a surface modification of the hydrophobic PDMS material to a reactive and hydrophilic SiO_x layer under ambient conditions with short reaction times is desirable. For this purpose excimer lamps, which provide high-intensity, high-efficiency, and narrow-band radiation, may be appropriate. Recent applications of excimer lamps include photodeposition of large area or patterned thin metal films,^{20,21} photoassisted low-temperature oxidation of Si,²² SiGe,²³ and Ge,²⁴ UV curing,²⁵ polymer etching, and microstructuring of polymer surfaces.^{26,27}

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(1) Gorur, R.; Cherney, E.; Burnham, J. *Outdoor Insulation*; College of Engineering and Applied Science, Arizona State University: Tempe, AZ, 1998.

(2) Campbell, B. *Dow Corning Corp. Pap.* **1996**.

(3) Rahimi, A.; Shokrolahi, P. *Int. J. Inorg. Mater.* **2001**, *3*, 843–847.

(4) Reller, A.; Braungart, M.; Soth, J.; von Uexküll, O. *Gaia* **2000**, *9*, 13–24.

(5) Seyferth, D. *Organometallics* **2001**, *20*, 4978–4992.

(6) Burkus, F. S.; II; Amarasekera, J. *Rubber World* **2000**, *222*, 26–35.

(7) Hill, R. M. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 255–261.

(8) Oestreich, S.; Struck, S. *Macromol. Symp.* **2002**, *187*, 333–342.

(9) Gill, I.; Ballesteros, A. *Trends Biotechnol.* **2000**, *18*, 469–479.

(10) Abbasi, F.; Mirzadeh, H.; Katbab, A.-A. *Polym. Int.* **2001**, *50*, 1279–1287.

(11) Hillborg, H.; Ankner, J. F.; Gedde, U. W.; Smith, G. D.; Yasuda, H. K.; Wikstrom, K. *Polymer* **2000**, *41*, 6851–6863.

(12) Holländer, A.; Klemberg-Sapieha, J. E.; Wertheimer, M. R. *J. Polym. Sci., Part A* **1995**, *33*, 2013–2025.

(13) Holländer, A.; Klemberg-Sapieha, J. E.; Wertheimer, M. R. *J. Polym. Sci., Part A* **1996**, *34*, 1511–1516.

(14) Fozza, A. C.; Roch, J.; Klemberg-Sapieha, J. E.; Kruse, A.; Holländer, A.; Wertheimer, M. R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1997**, *131*, 205–210.

(15) Ouyang, M.; Yuan, C.; Muisener, R. J.; Boulares, A.; Koberstein, J. T. *Chem. Mater.* **2000**, *12*, 1591–1596.

(16) Kim, J.; Chaudhury, M. K.; Owen, M. J. *J. Colloid Interface Sci.* **2000**, *226*, 231–236.

(17) Graubner, V.-M.; Jordan, R.; Nuyken, O.; Kotz, R.; Lippert, T.; Schnyder, B.; Wokaun, A. *Polym. Mater. Sci. Eng.* **2003**, *88*, 488–489.

(18) Graubner, V.-M.; Jordan, R.; Nuyken, O.; Schnyder, B.; Lippert, T.; Kotz, R.; Wokaun, A. *Macromolecules* **2004**, *37*, 5936–5943.

(19) Schnyder, B.; Lippert, T.; Koetz, R.; Wokaun, A.; Graubner, V.-M.; Nuyken, O. *Surf. Sci.* **2003**, *532–535*, 1067–1071.

(20) Esrom, H. *Appl. Surf. Sci.* **2000**, *168*, 1–4.

(21) Boyd, I. W.; Zhang, J. Y.; Bergonzo, P. *Proc. SPIE—Int. Soc. Opt. Eng.* **1995**, *2403*, 290–301.

(22) Kaliwot, N.; Zhang, J. Y.; Boyd, I. W. *Appl. Surf. Sci.* **2000**, *168*, 288–291.

This paper presents data obtained by neutron reflectometry together with spectroscopic ellipsometry on cross-linked PDMS surfaces after irradiation with a Xe₂*-excimer lamp at 172 nm. As nondestructive methods, neutron reflectometry and spectroscopic ellipsometry are powerful tools for the investigation of the surface and bulk properties of polymer films at ambient conditions. In neutron reflectometry, the incident neutrons are electrically neutral and are scattered at the nuclei, and variations in scattering length density are detected as a function of sampling depth. The technique provides subnanometer resolution with penetration depths of hundreds of nanometers. Ellipsometry probes the change of the polarization state upon reflection. This allows determining the optical properties of untreated and irradiated PDMS films.

Experimental Section

Materials. Films of cross-linked PDMS were prepared by spin-coating of a solution of vinyl-functionalized poly(dimethylsiloxane), poly(methylhydrosiloxane) as a cross-linker and a Karstedt platinum catalyst in isooctane on silicon wafers. To obtain different thicknesses the solution concentration (1–6.5 wt %) and/or the rotation speed (1500–7000 rpm) were varied. The size of the silicon wafers were ~1 cm in diameter for the ellipsometric measurements and 10 cm in diameter for the neutron reflectometry measurements. The films were cured for 5 min at 100 °C after evaporation of the solvent, resulting in film thicknesses from 50 to 730 nm.

UV Source. Exposure to vacuum ultraviolet (VUV) light was performed with a water-cooled Xe₂*-excimer lamp emitting at a wavelength of 172 nm. The experimental setup is described elsewhere.^{18,28} The PDMS samples were irradiated at ambient conditions in air with intensities of 10.4 and 16.6 mW/cm² at a distance of 5 mm to the UV source.

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 photon energies were scanned from 1.5 to 4.5 eV in 0.05 eV intervals. The ellipsometer records tan(Ψ) and cos(Δ) as a function of energy (wavelength) using the Hadamard transformation of the photodetected signal.

Neutron Reflectometry. Neutron reflectometry experiments were performed at the Apparatus for Multi Option Reflectometry (AMOR) at the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institute in Villigen, Switzerland. The measurements were performed in the time-of-flight modus and the wavelength of the cold neutrons was varied between 0.13 and 1.3 nm. The experimental setup is described in detail elsewhere.^{29–31} Data evaluation and modeling were performed with the fitting program Parratt32, version 1.5.2.^{32–34}

Theoretical Basis

Neutron Reflectometry. Neutron reflectometry is a nondestructive method for the analysis of thin single- and

multilayers. The data that can be obtained upon analysis are: the layer thickness, roughness, scattering length density, inter diffusion parameters and magnetic moments within the layers and at the interfaces.

The reflectivity R measured exhibits a dependence of the neutron momentum transfer normal to the surface q that follows very closely q^{-4} dependence characteristic of simple sharp interfaces. When a layer is located on the surface the interference of the neutrons scattered at the air/polymer and the polymer/Si-substrate interfaces gives rise to a series of pronounced maxima and minima in R as a function of q (Kiessig oscillations). The distance between two maxima, Δq , is only dependent on the film thickness d , viz. $\Delta q = 2\pi/d$.³⁵ The thickness and scattering length density nb of that layer can be derived from a quantitative analysis of the reflectivity curves $R(q)$.

The scattering length density nb of a polymer is derived from the bound coherent scattering length b of a polymer which is calculated from the repeating unit with the following equation (x_i , number of atoms of the element i ; b_i , bound coherent scattering length of the atoms of the element i):

$$b = \sum_i x_i b_i. \quad (1)$$

For the bound coherent scattering length of PDMS (repeating unit $-\text{SiO}(\text{CH}_3)_2-$) $b_{\text{PDMS}} = 0.810$ fm ($b_{\text{C}} = 6.6460$ fm, $b_{\text{Si}} = 4.1491$ fm, $b_{\text{O}} = 5.8030$ fm, and $b_{\text{H}} = -3.7390$ fm) is applied.¹¹ The atoms in the cross-links and the end groups of the polymer are neglected. The scattering length density (nb) at the critical angle for total reflection (ϑ_c) is defined as³⁶

$$nb = \frac{q_c^2}{16\pi} \quad (2)$$

q_c is the neutron momentum transfer normal to the surface at the critical angle of total reflection and n is the atomic density of the repeating units in the polymer which is defined by

$$n = \frac{\rho N_A}{M} \quad (3)$$

ρ is the density of the polymer (0.4275 g/cm³), N_A the Avogadro constant and M the molar mass of the repeating unit (74.1545 g/mol).

Results and Discussion

Spectroscopic Ellipsometry.¹⁹ Spectroscopic ellipsometry (SE) is a well-known technique for the analysis of thin films^{37,38} and can be utilized to determine the film thicknesses and optical properties of films in stratified layer systems. For transparent films ($k = 0$) on a known substrate it is possible to determine the film thickness and the refractive index n simultaneously. The changes of the refractive index and of the polymer film thickness induced by the UV-irradiation were analyzed since PDMS and the SiO_x, which is generated during the UV-irradiation, are transparent. The apparent thickness is the result of the data analysis with a single layer model. The substrate was crystalline silicon. The native oxide layer

(23) Zhang, J.-Y.; Fang, Q.; Kenyon, A. J.; Boyd, I. W. *Appl. Surf. Sci.* **2003**, *208–209*, 364–368.

(24) Craciun, V.; Hutton, B.; Williams, D. E.; Boyd, I. W. *Electron. Lett.* **1998**, *34*, 71–72.

(25) Zhang, J.-Y.; Windall, G.; Boyd, I. W. *Appl. Surf. Sci.* **2002**, *186*, 568–572.

(26) Zhang, J.-Y.; Boyd, I. W.; Esrom, H. *Surf. Interface Anal.* **1996**, *24*, 718–722.

(27) Zhang, J. Y.; Esrom, H.; Kogelschatz, U.; Emig, G. *Appl. Surf. Sci.* **1993**, *69*, 299–304.

(28) Gellert, B.; Kogelschatz, U. *Appl. Phys. B: Laser Opt.* **1991**, *52*, 14–21.

(29) Clemens, D.; Gross, P.; Keller, P.; Schlumpf, N.; Konnecke, M. *Physica B* **2000**, *276–278*, 140–141.

(30) Clemens, D. *Physica B* **1996**, *221*, 507–513.

(31) Clemens, D. *PSI-Proc.* **1996**, *96–02*, 65–77.

(32) Névoit, L.; Croce, P. *Rev. Phys. Appl.* **1980**, *15*, 761–779.

(33) Parrat, L. G. *Phys. Rev.* **1954**, *95*, 359–369.

(34) Press, W.; Flannery, B.; Teukolsky, S.; Vetterling, W. *Numerical Recipes*; Cambridge University Press: Cambridge, U.K., 1986.

(35) Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171–271.

(36) Klein, A. G.; Werner, S. A. *Rep. Prog. Phys.* **1983**, *46*, 259–335.

(37) Tompkins, H. G.; McGahan, W. A. *Spectroscopic Ellipsometry and Reflectometry*; John Wiley & Sons: New York, 1999.

(38) Azzam, R. M. A.; Bashara, N. N. *Ellipsometry and Polarized Light*; North-Holland Publ. Co.: Amsterdam, 1989.

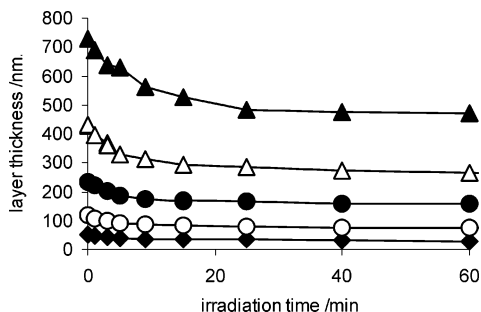


Figure 1. Change of the layer thickness of several PDMS films on silicon substrate as a function of the irradiation time (intensity 16.6 mW/cm²). Layer thicknesses before irradiation: (◆) 52, (○) 118, (●) 232, (△) 429, and (▲) 729 nm.

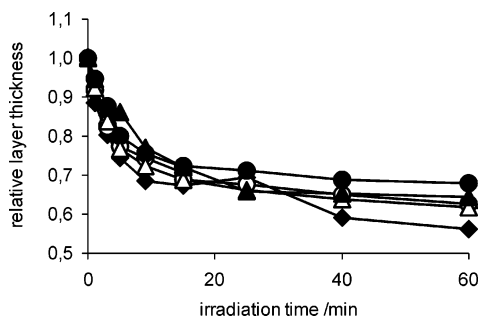


Figure 2. Change of the relative layer thickness of several PDMS films on silicon substrate as a function of the irradiation time (intensity 16.6 mW/cm²). Layer thicknesses before irradiation: (◆) 52, (○) 118, (●) 232, (△) 429, and (▲) 729 nm.

(~2 nm) on top of the silicon wafer was not included in the model. In general SE is rather sensitive to small changes in the refractive index and/or layer thickness. However, in the case of stratified layers the correlation between refractive index n and layer thickness d is significant and small changes of n may be compensated by changes of d . The refractive indices of PDMS (1.405) and SiO₂ (1.457³⁹) are very similar; therefore, applying a multilayer model is not very reasonable, and the analysis was limited to a single layer model.

For the measurements, films with various thicknesses were produced to test the reproducibility of the irradiation and analysis and to analyze the influence of the starting film thickness. The changes of the film thickness of five different PDMS films irradiated with the Xe₂*-excimer lamp at the same intensity (16.6 mW/cm²) are shown in Figure 1.

The decrease of the film thickness appears to be exponential for all films and the curves are very similar when the changes in the relative (normalized) film thickness are plotted as a function of the irradiation time (Figure 2). This suggests that up to a layer thickness of 730 nm the changes in the relative layer thickness with irradiation are independent of the starting layer thickness. This would indicate that the modification of the PDMS with irradiation is constant throughout the whole layer thickness, which is different to the data modeling of the neutron reflectometry data, which will be discussed in detail below. It is noteworthy to mention that the ellipsometry results were produced by applying a single layer model, which is probably not correct. However, as discussed above, a multilayer model would not be useful due to the lower sensitivity of this method.

(39) *Handbook of Optical Constants of Solids*; Palik, E. D., Ed.; Academic Press: 1985 and 1991; Vols. 1 and 2.

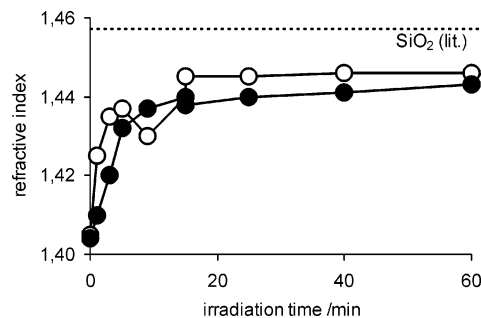


Figure 3. Change of the refractive index ($\lambda = 620$ nm) as a function of irradiation time. Layer thicknesses before irradiation: (○) 118 and (●) 232 nm.

Within the first 10 min of irradiation the layer thickness decreases by roughly 30% in average. This initial fast decrease is followed by a slower decrease and after 60 min of irradiation the change approaches a relative layer thickness of 55–70% compared to the initial layer thickness. The theoretical change of the layer thickness for a complete transformation of PDMS into silicon oxide is 55%,⁴⁰ which could be achieved since the relative amount of silicon in the surface does not change upon irradiation as derived from XPS analysis.¹⁸ The decrease of the layer thickness with irradiation is due to material removal and/or an increase of the density during the transformation of the organic siloxane into inorganic silicon oxide. Koberstein et al. probed the changes in the layer thickness of PDMS layers after exposure to UV/ozone (low-pressure mercury-quartz lamp, 185–254 nm) by spectroscopic ellipsometry and applying a single layer model likewise.¹⁵ They observed an absolute thickness decrement of about 75 nm (initial layer thickness of 400–1000 nm) after 120 min of exposure. This comparatively low thickness decrement is probably due to the UV light with higher wavelength and less intensity of the lamp Koberstein et al. used in their irradiation experiments.

The changes of the refractive index n show an opposite trend (Figure 3) to the changes in the layer thickness with irradiation, i.e., an increase with increasing irradiation time.

For untreated PDMS the corresponding value of n is 1.405 at 2 eV ($\lambda = 620$ nm) which increases to 1.44 within 15 min of irradiation and reaches a plateau of 1.446 after 60 min of exposure. This value is quite close to the literature value of the refractive index for SiO₂ which is 1.457³⁹ ($\lambda = 620$ nm) and reveals the formation of a silica like surface with irradiation.

Chemical Composition of the Oxidized Surface Layer. Figure 4a shows the neutron reflectivity R as a function of q for unexposed spin-coated PDMS. The calculated scattering length density of unoxidized PDMS is $0.03 \times 10^{-4}/\text{nm}^2$ while the silicon substrate has an nb value of $2.07 \times 10^{-4}/\text{nm}^2$. The experimental data were evaluated by using a 2-layer model with PDMS as the first layer using a thickness of 113 nm (determined by ellipsometry) and the natural silicon oxide on the silicon wafer as the second layer (2 nm as determined by ellipsometry) with air and silicon substrate as boundaries (Figure 4a). The insert in the figure shows the profile of the scattering length density as a function of layer depth. The figure reveals a very tiny step in nb at $z = 0$, displaying the very small scattering length density contrast between air and PDMS. This leads to the smooth character of the log $R(q)$ curve, showing no oscillations by the PDMS layer.

(40) Muisener, R. J. Dissertation, University of Connecticut, 1999.

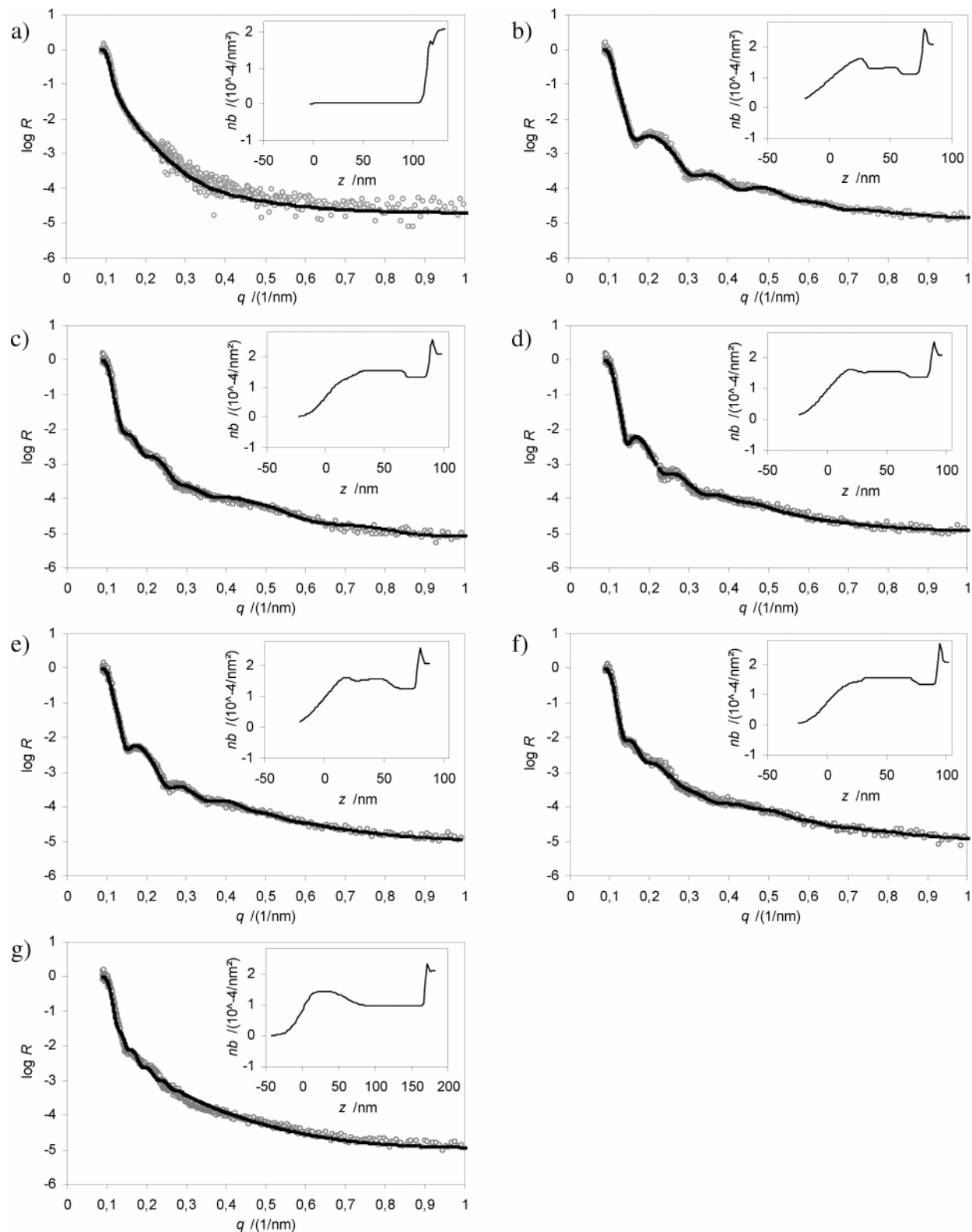


Figure 4. Neutron reflectivity as a function of the scattering vector. The inset figures show the profile of the scattering length density (nb) as a function of the layer depth (z). The continuous lines displayed in parts a–g show the best fits to the experimental data (circles): (a) unexposed specimen, 115 nm; (b) 91 nm, 16.6 mW/cm^2 , 5 min (layer thickness of specimen before irradiation, intensity of irradiation, irradiation time); (c) 115 nm, 16.6 mW/cm^2 , 2 min; (d) 115 nm, 16.6 mW/cm^2 , 5 min; (e) 115 nm, 16.6 mW/cm^2 , 10 min; (f) 115 nm, 10.4 mW/cm^2 , 5 min; (g) 200 nm, 16.6 mW/cm^2 , 5 min.

Thus, it is not possible to determine the thickness of the spin-coated PDMS layer by neutron reflectometry and it is impossible to define a surface roughness. Varying the surface roughness between 0 and 113 nm (thickness of the PDMS layer) did not reveal any significant changes in the data fitting.

The irradiated samples reveal several oscillations in the reflectivity as a function of q (Figure 4b–g). The oscillations characterize layers with different scattering length densities (i.e., different chemical composition and/or density) than of unoxidized PDMS. The amplitude of the oscillations is more pronounced, when the difference

Table 1. Layer Thickness of the Complete Layer (d_0) before Irradiation, Irradiation Intensity (I), Irradiation Time (t), and Modeling Parameters after Irradiation of Samples in Figure 4b–g^a

Figure	4b	4c	4d	4e	4f	4g
$I/(mW/cm^2)$	16.6	16.6	16.6	16.6	10.4	16.6
t/min	5	2	5	10	5	5
d_0/nm	91	115	115	115	115	200
d_i/nm	78	91	87	81	96	172
d_i/d_0	0.86	0.79	0.76	0.71	0.83	0.86
d_{i1}/nm	30	26	23	22	30	20
d_{i2}/nm	27	42	41	34	43	40
d_{i3}/nm	20	21	22	23	20	110
d_{SiO_2}/nm	2	2	2	2	2	2
$nb_1/(10^{-4} nm^{-2})$	1.82	1.35	1.87	1.91	1.46	1.65
$nb_2/(10^{-4} nm^{-2})$	1.32	1.54	1.56	1.58	1.56	1.45
$nb_3/(10^{-4} nm^{-2})$	1.12	1.32	1.36	1.26	1.35	0.95
σ_1/nm	20	11	15	16	13	15
σ_2/nm	3	4	4	3	1	5
σ_3/nm	2	1	3	4	2	15
σ_{SiO_2}/nm	2	2	2	2	1	2

^a Layer thickness of the whole layer (d_i) and of the single model layers (d_{i1} to d_{i3} , d_{SiO_2}), scattering length density of the single model layers (nb_1 to nb_3) and the roughness of the single model layers (σ_1 to σ_3 , σ_{SiO_2}) obtained from the modeling of the data in Figure 4b–g.

in the scattering length density between the layers is enhanced. A high roughness at the interface has an opposite effect, i.e., it blurs the oscillations and they are less distinct. The roughness is a function of the surface roughness of the polymer, the surface roughness of the substrate and the roughness of the interface between oxidized and unoxidized layer over the whole spin-coated silicon wafer.

Different from data described by Hillborg et al.,¹¹ it was not possible to apply a 2-layer model only consisting of an oxidized layer at the surface with a rough interface to the unoxidized PDMS on the silicon substrate. In our case it was necessary to apply a 4-layer model which resulted in satisfying modeling of the data. This model includes 3 layers of oxidized PDMS of different scattering length densities and one layer of the 2 nm native silicon oxide on the silicon substrate. The resulting parameters (layer thickness, scattering length density, and roughness) are summarized in Table 1.

The modeling of the neutron reflectometry data for irradiated samples with smaller initial layer thickness (91 and 115 nm, Figure 4b–f) agree very well with the experimental data, while it was impossible to obtain satisfying fits to the experimental data for samples with thicker initial layer thickness (200 and 260 nm). In Figure 4g the fit of the irradiated sample with an initial layer thickness of 200 nm is shown as an example. The pronounced deviation between the model and the data are probably due to lateral differences in the thickness of the spin-coated PDMS layer of up to 30 nm which is much larger than the maximum deviation of 10 nm for thinner PDMS films, which is discussed in the next section.

The scattering length densities of the area closest to the surface (thickness of first model layer ≤ 30 nm) have values between 1.3×10^{-4} and $2.0 \times 10^{-4} nm^{-2}$ for all samples (Figure 4b–g). The variation of this value is in the range of $\leq 10\%$. This corresponds most probably to the substitution of one to two methyl groups at the silicon (Table 2) by oxygen and correlates very well with the data from the XPS analysis, which shows that within 5 min of irradiation at 16.6 mW/cm² the ratio of oxygen to silicon reaches a value of 1.8,^{18,19} which corresponds to a mixture of $-Si(CH_3,OH)O-$ and $-Si(OH)_2O-$ within the 5 nm sampling depths of XPS (Table 2). With decreasing intensity and irradiation time, less substitution of methyl

Table 2. Scattering Length Densities of Different Repeating Units^a

repeating unit	$nb/10^{-4}nm^{-2}$	$\rho/(g/cm^3)$
$-Si(CH_3)_2O-$	0.03	0.43 ^b
$-Si(CH_3,OH)O-$	1.15 ¹¹	1.40 ¹¹
$-Si(OH)_2O-$	1.85 ¹¹	1.70 ¹¹
$-SiO_2-$	3.48 ^c	2.20 ^c
$-Si-$	2.07 ^c	2.33 ^c

^a The structures are based on reported data of the chemical changes in PDMS irradiated with the Xe₂*-excimer lamp.¹⁸ ^b The density of PDMS has been experimentally determined to 0.43 g/cm³. ^c The scattering length densities and the densities were given from the fitting program Parrat32.

groups by oxygen occurs resulting in smaller scattering length densities. The chemical mechanism of PDMS oxidation by 172 nm irradiation in air was recently summarized.¹⁸

At depth greater than 30 nm within the films less methyl groups are substituted by oxygen which is supported by lower values of the scattering length density in the second model layer. This trend continues for layers further inside the film, e.g., the third model layer, and an overall decrease of the scattering length density and therefore the grade of oxidation is dependent on the amount of “reactive” oxygen available below the surface. The degree of the substitution of methyl groups by oxygen is decreasing with increasing layer depth, probably due to hindered diffusion of oxygen and reactive oxygen into the deeper layers depth through the previously formed silicon oxide layer. This general trend is not observed for short irradiation times (Figure 4c) and low irradiation intensities (Figure 4f). A slight increase in the scattering length density in the second model layer compared to the first model layer is detected in these cases. This is probably due to hydrophobic recovery (the total time frame from irradiation to the end of the neutron reflectometry is about 8–10 h), which has already been observed during contact angle measurements,⁴¹ where an increase of the water contact angle with increasing storage time was observed. Recent publication stated that the hydrophobic recovery after treatment with partial electrical discharges^{16,42–44} and plasmas^{11,45} and after environmental degradation⁴⁶ can be mainly assigned to the diffusion of linear and/or cyclic low molecular weight species, which were generated by the oxidation process. The processes of minor importance include the reorientation of polar groups from the surface into the bulk and reorientation of nonpolar groups from the bulk to the surface, respectively as well as the condensation of the surface hydroxyl groups.

Roughness of the Surface and the Interfaces. The roughness of the first interface, i.e., between air and the first model layer (σ_1) in the samples of Figure 4b–f is relatively high (11–20 nm) compared to the layer thickness of the first model layer (20–30 nm) and the roughness of the interfaces below the surface (1–5 nm). The oxidation of the surface is accompanied by a loss of material and a densification of the remaining material, which may increase the roughness at the air – oxidized material interface. The oxidation process results in a relatively

(41) Graubner, V.-M. Dissertation, Technische Universität München, 2004.

(42) Hillborg, H.; Gedde, U. W. *Polymer* **1998**, *39*, 1991–1998.

(43) Hillborg, H.; Sandelin, M.; Gedde, U. W. *Polymer* **2001**, *42*, 7349–7362.

(44) Hillborg, H.; Karlsson, S.; Gedde, U. W. *Polymer* **2001**, *42*, 8883–8889.

(45) Fritz, J. L.; Owen, M. J. *J. Adhes.* **1995**, *54*, 33–45.

(46) Hunt, S. M.; George, G. A. *Polym. Int.* **2000**, *49*, 633–635.

high surface roughness and distinct layers of oxidized PDMS within the film.

Pronounced oscillations in the reflectivity curves suggest that the roughness of the interfaces below the surface is relatively small and the differences in the scattering length densities of the different model layers are relatively high. Less pronounced oscillations are due to a higher roughness and/or less contrast. For the samples in Figure 4, parts b and d–e (initial layer thickness of 91 and 115 nm) the scattering length density difference is relatively high compared to the roughness of the interfaces (σ_1 to $\sigma_3 = 1\text{--}20$ nm) and the differences of the total layer thickness (5–10 nm). The changes in the scattering length densities from model layer one (nb_1) to model layer three (nb_3) are in the range of 30 to 40% and the oscillations are clearly visible. For the samples in Figure 4, parts c and f (initial layer thickness of 115 nm) the change of the scattering length density from model layer one (nb_1) to model layer three (nb_3) is within the estimated error range of 10% and is about 10 to 13% higher in the second model layer (nb_2), which is as discussed above most probable due to lower irradiation time and intensity and hydrophobic recovery. The scattering length density difference for the samples in Figure 4, parts c and f is less significant as for the samples in Figure 4, parts b and d–e, but the parameters for the roughness of the interfaces are more or less constant for all samples, which results in less visible oscillations for the samples in Figure 4, parts c and f.

The reflectivity curve of the sample in Figure 4g significantly differs from the curves in Figure 4b–f. The oscillations in the reflectivity are very small. The initial layer thickness is two times larger than in the case of the other samples and the lateral variation of the total layer thickness is about 30 nm over the whole spin-coated wafer. This variation of the thickness results in the superposition of reflectivity curves of areas with different total layer thicknesses and different roughnesses of the interfaces. The resulting reflectivity data can therefore not be fitted to an appropriate model although the contrast in the scattering length densities should at least reach the same level as for the data in Figure 4d (same irradiation time and intensity). The fitted model suggests a change of about 42% from nd_2 to nd_3 .

Comparison between Spectroscopic Ellipsometry and Neutron Reflectometry Analysis. As mentioned before the SE results for PDMS films of various thicknesses implied that the changes within the polymer film are constant throughout the whole layer thickness. This is indeed in contrast to the quite evident changes in the scattering length density within the film. Upon inspection the relative changes of the scattering length density and the relative changes of the optical density—as expressed by the refractive index n —it becomes evident that the contrast between various layers is much higher for the neutron reflectometry method. The changes in nb within the modified film are on the order of 20–70%. The changes in nb from the unmodified to the modified film are even higher (0.03 compared to $1.8 \times 10^{-4} \text{ nm}^{-2}$).

On the other hand, the changes in the refractive index of the unmodified film compared to the modified film are on the order of 4% only. Within a modified film the variations in n are expected to be even lower, most certainly below 1%, because the neutron reflectometry data clearly show that the film is indeed modified throughout its thickness. In addition, already Greef⁴⁷ had mentioned that ellipsometry is not very sensitive to the value of n in the case of very thin films, because thickness

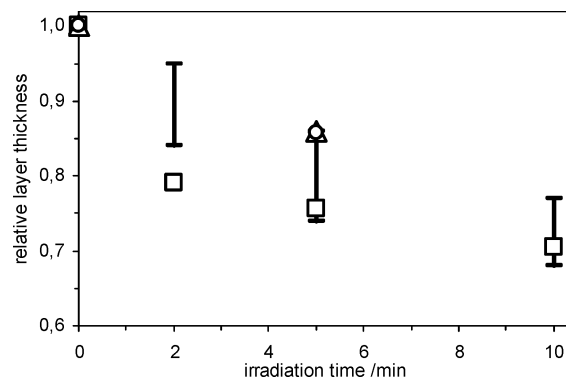


Figure 5. Change of the relative layer thickness with irradiation time (intensity 16.6 mW/cm^2) of PDMS films with different initial layer thicknesses: (○) 91, (□) 115, (△) 200 nm. The black bars represent the range of the relative layer thicknesses calculated from spectroscopic ellipsometry at the same irradiation time (initial layer thickness 52–729 nm, 16.6 mW/cm^2). The relative layer thickness of PDMS films with an initial layer thickness of 91 and 200 nm are lying on top of each other after 5 min irradiation time.

and refractive index are highly correlated in the calculations. Hence the refractive index and thickness should actually be measured independently. Therefore, we assume that SE is not a convenient technique to resolve the density changes within the film and a single layer model is the best approximation for this system.

Thickness of the Oxidized Surface Layer. The comparison of the total layer thicknesses before (d_0) and after irradiation (d_t) obtained from the 4-layer model for the neutron reflectometry data is compiled in Table 1.

An overall decrease in the layer thickness is observed with increasing irradiation time and/or increasing intensity. The changes in the layer thickness are conforming to the data from the ellipsometric measurements (shown in Figure 5). The black bars represent the range of the relative layer thickness calculated from spectroscopic ellipsometry (Figure 1) at the same irradiation time and intensity (16.6 mW/cm^2).

The relative layer thickness obtained by ellipsometry reaches a value between 0.74 and 0.86 after 5 min of irradiation at 16.6 mW/cm^2 . All total layer thicknesses (same irradiation intensity and time) obtained from the modeling of the neutron reflectometry data from Figure 4, parts b, d, and g, are within this range. The relative layer thickness is between 0.67 and 0.76 (from ellipsometry) and 0.70 (from the neutron reflectometry data in Figure 4e) after 10 min of irradiation at 16.6 mW/cm^2 . Only after an irradiation time of 2 min a clear difference between the data from the two methods is obtained. The relative layer thickness from ellipsometry has a value between 0.84 and 0.95 while the value from neutron reflectometry is 0.79, but they are still within the error range of 10%. The data from both methods are comparable for an initial film thickness of 91, 113, or 200 nm although the ellipsometry data were evaluated by applying a single layer model. The decrease of layer thickness with irradiation time is, as already discussed, due to material loss on the surface and/or an increase of the density during the transformation of the organic siloxane into the inorganic silicon oxide.

Conclusion. Irradiation of PDMS at 172 nm under ambient conditions results in a rapid and controllable surface oxidation of the polymer. A silicon oxide layer is formed with a surface roughness of 11–20 nm. Ellipsometric and neutron reflectometry measurements showed that the total layer thickness decreases to about 70%

within the first 10 min of irradiation and seems to reach a final value of about 50–60% on further irradiation, which is very close to the theoretical value of 50% for a complete transformation of PDMS to SiO₂. The refractive index determined by ellipsometry also reaches a value, which is very close to n of SiO₂.

The more sensitive neutron reflectometry measurements reveal that the oxidized layer is not of uniform composition and cannot be interpreted as a homogeneous silicon oxide layer. A four-layer model has been applied, which uses three layers of differently oxidized PDMS and one layer natural silicon oxide on the silicon wafer. The degree of oxidation is increasing with increasing irradiation time and intensity. The material close to the air interface consists mainly of $-\text{Si}(\text{OH})_2\text{O}-$ after 5–10 min of irradiation with 16.6 mW/cm². The degree of the

substitution of methyl groups by oxygen is decreasing with increasing layer depth, probably due to diffusion of a lower amount of reactive oxygen into increasing layer depth. This is confirmed by the lower scattering length density than in the surface near areas which can be assigned to a mixture of $-\text{Si}(\text{CH}_3, \text{OH})\text{O}-$ and $-\text{Si}(\text{OH})_2\text{O}-$ species. The roughness of the surface is relatively high (11–20 nm) compared to the roughness of the interfaces (1–4 nm) within the oxidized PDMS layer.

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