

Thickness of SiO_x layers on poly (dimethylsiloxane) surfaces created by 172 nm irradiation in air studied by neutron reflectometry

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Spincoated specimens of crosslinked poly (dimethylsiloxane) (PDMS) films exposed to vacuum ultraviolet radiation $\lambda = 172$ nm (Xe₂*-excimer lamp) in air were studied by neutron reflectometry. The fit of the experimental data showed a significant decrease of the layer thickness. As previously revealed by XPS an oxidation of the polymer to inorganic SiO_x, i.e. silicon bonded to three or four oxygen atoms, is taking place. The loss of material and the densification of the surface material caused the decrease in surface layer thickness. The results correspond well with recently conducted ellipsometry measurements.

Poly (dimethylsiloxane) was irradiated under ambient conditions in air with a Xe₂*-excimer lamp ($\lambda = 172$ nm). Various intensities and irradiation times were applied. The formation of active oxygen and ozone with irradiation in air causes a surface oxidation of polydimethylsiloxane to SiO_x [1]. The irradiated surfaces were studied by neutron reflectometry on the apparatus for multi option reflectometry AMOR at SINQ/PSI.

Figure 1 shows the specular neutron reflectivity (R) as a function of neutron momentum transfer ($q=4\pi\sin\theta/\lambda$) for unexposed spin-coated PDMS. Fitting of the experimental data results in a layer thickness of 202 nm and a scattering length density (nb) for unoxidised PDMS of $0.06 \times 10^{-4} \text{ nm}^{-2}$ which corresponds well with the theoretically calculated nb value [2]. The inset in Figure 1 depicts the profile of the scattering length density as a function of layer depth (z). It shows a very tiny step in nb at $z = 0$. PDMS was almost indistinguishable from air.

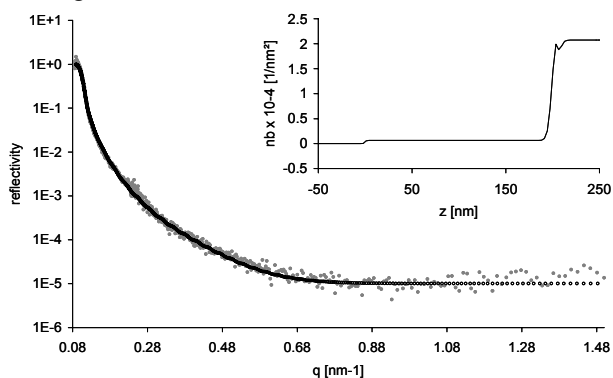


Figure 1: R as a function of q of an unexposed specimen (● experimental data, ○ best fit to the experimental data). The inset figure shows the profile of nb as a function of z of the unexposed specimen.

The samples exposed to 172 nm radiation in air showed distinct oscillations in the reflectivity as a function of q . One representative sample is shown in Figure 2. The oscillations characterize a layer with different scattering length density (i.e. a different chemical composition) than for unoxidised PDMS that appeared in the samples after irradiation. The spacing between successive ripples can be used to estimate the thickness of this layer: $d \approx 2\pi/\Delta q$. For the sample in Figure 2 the initial layer thickness of the unexposed specimen was ~ 202 nm, after irradiation (16.6

mW/cm², 5 min) the layer thickness was reduced to 144 nm. This value corresponds very well with the data retrieved by ellipsometry measurements published recently [1].

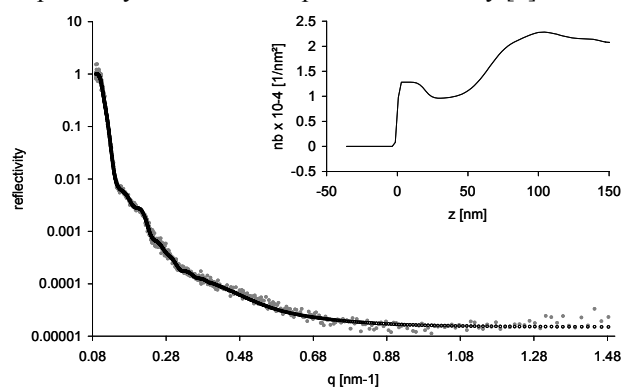


Figure 2: R as a function of q for an irradiated specimen (2.8 mW/cm², 5 min), (● experimental data, ○ best fit to the experimental data). The inset figure shows the profile of nb as a function of z of the irradiated sample. Initial thickness of the PDMS layer: 202 nm; thickness of the oxidized layer: 144 nm.

Furthermore the fitting of the experimental data shows that the layer has not been uniformly transformed over its full thickness as can be clearly seen in the depth profile of nb (Figure 2). One possibility for the observed changes of the nb value is an increase of the oxygen content with increasing thickness. This is improbable because diffusion of active oxygen and ozone is becoming less with increasing layer depth and XPS data showed a transformation of the polymer to SiO₂ [1] on the surface. Therefore we suggest that the observed change in the nb value is due to an increase of density of the transformed material with increasing layer depth (the scattering length density is proportional to the density of the material).

- [1] B. Schnyder, T. Lippert, R. Kötz, A. Wokaun, V.-M. Graubner, O. Nuyken, *Surface Science* **532-535**, 1067 (2003).
- [2] H. Hillborg, J.F. Ankner, U.W. Gedde, G.D. Smith, H.K. Yasuda, K. Wikström, *Polymer* **41**, 6851 (2000).

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