

# In-line monitoring of the thickness of silica and silazane layers in the submicron range by NIR reflection spectroscopy

Tom Scherzer,\* Katja Heymann, Gabriele Mirschel and Lutz Prager

*Leibniz Institute of Surface Modification (IOM), Permoserstr. 15, D-04318 Leipzig, Germany. E-mail: tom.scherzer@iom-leipzig.de*

## Introduction

Polysilazanes such as perhydropolysilazane (PHPS) may be used as precursors for thin silica-based gas barrier layers, that have to be deposited on heat-sensitive substrates (e.g. polymer foils) at rather low temperatures. Such coatings might be used for packaging applications and as protective coatings, but also for high-tech products such as flexible solar cells and organic light-emitting diodes (OLEDs). The most common pathway to transform PHPS into  $\text{SiO}_x$  is thermal conversion. Alternatively, PHPS can be converted into  $\text{SiO}_x$  by irradiation in the vacuum ultraviolet (VUV) in the presence of oxygen.<sup>1,2</sup> For use in commercial applications, a technology for the continuous application of PHPS to polymer foil and its photochemical conversion to  $\text{SiO}_x$  has been developed.<sup>2</sup> The coating process is carried out by slit nozzle coating using a pilot scale coating line, which is equipped with  $\text{Xe}_2^*$  excimer VUV lamps.

The gas barrier properties of  $\text{SiO}_x$  coatings strongly depend on the thickness and the uniformity of the deposited layers. Therefore, continuous monitoring of the coating by an appropriate sensor system is necessary in order to avoid accidental and systematic deviations from the nominal value. It has been shown recently, that NIR reflection spectroscopy can be used for in-line monitoring of the conversion and the thickness of thin acrylate and epoxy coatings with a thickness of about 5 to 50  $\mu\text{m}$ .<sup>3,4</sup> In the present study, we will show that this method is also suited for monitoring of the thickness of silica and silazane layers, although their thickness is about two orders lower than the thickness of the acrylate coatings.

## Experimental

Polysilazane layers for laboratory investigations were applied by spin-coating of a 3 % solution of PHPS (Clariant) in dibutyl ether, either to silicon wafers or to 23  $\mu\text{m}$  PET (polyethylene terephthalate) foil. In order to vary the thickness of the coatings, different rotation speeds between 800 and

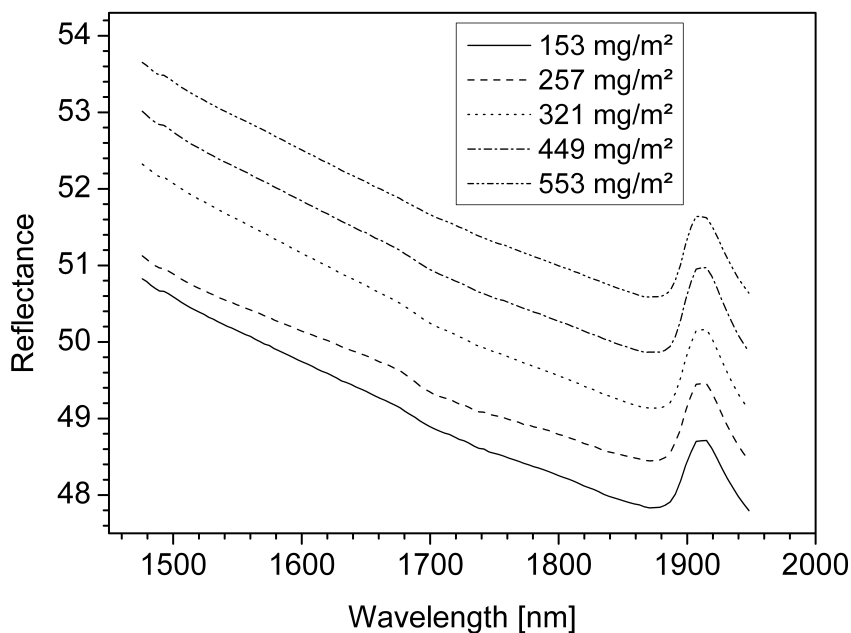


Figure 1. NIR spectra of PHPS layers on silicon wafers.

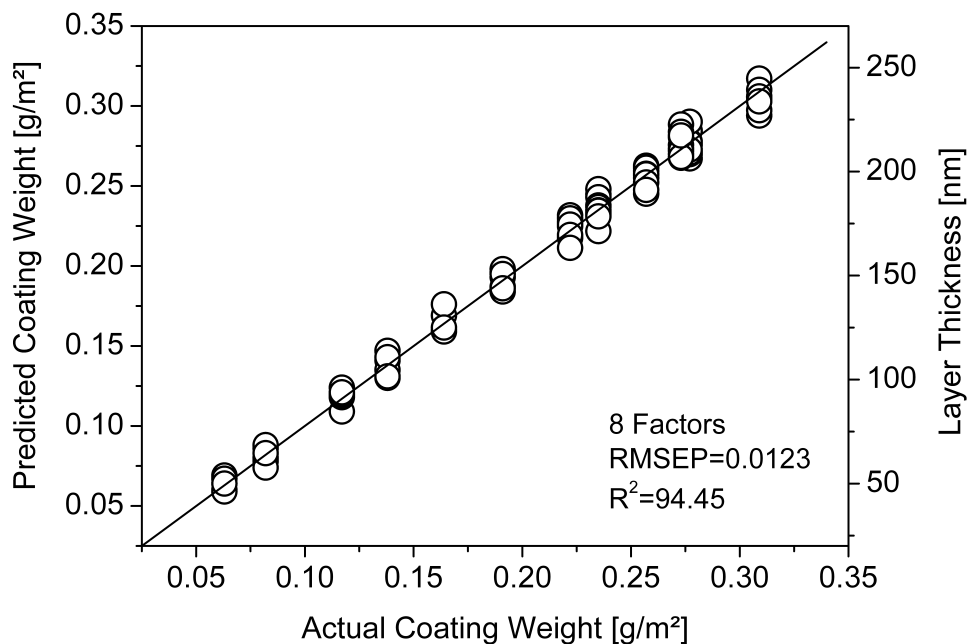


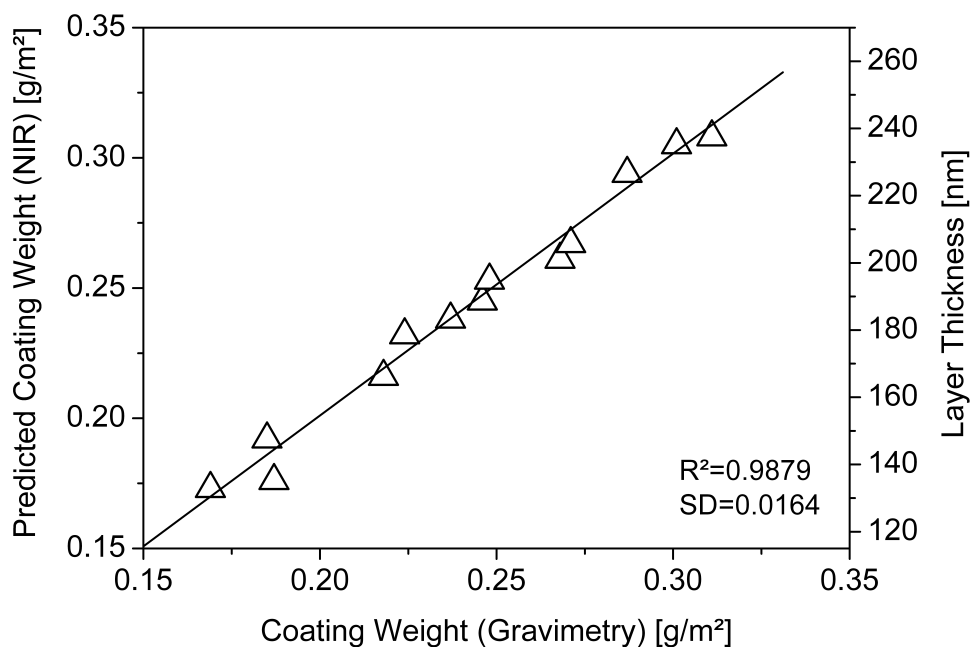
Figure 2. PLS calibration of the reflectance spectra of PHPS coatings on PET foil to their coating weight. The thickness was estimated from the coating weight ( $\rho = 1.3 \text{ g cm}^{-3}$ ).

4000 rpm were used, and up to three layers were applied. After drying at room temperature, the NIR spectrum of the sample was recorded, and its coating weight was determined by gravimetry. Then, PHPS was converted into  $\text{SiO}_x$  by VUV irradiation at 172 nm using a  $\text{Xe}_2^*$  excimer lamp (Heraeus Noblelight). Afterwards, NIR spectrum and coating weight were measured again.

Continuous application of PHPS to PET foil was carried out with a pilot-scale coating machine by use of a slit nozzle (Coatema) at a line speed of  $7.5 \text{ m min}^{-1}$ . The slit nozzle was fed by a gear pump, which allows systematic variation of the thickness of the layer. The actual thickness was calculated from the material flow through the calibrated slit nozzle. After infrared drying, the layer was irradiated with VUV radiation. A more detailed description of the pilot-scale coating trials is given in Reference 5.

NIR spectra were recorded with a process spectrometer, which was developed by LLA Instruments for investigations on thin polymer coatings.<sup>6</sup> It consists of a spectrometer unit based on an InGaAs photodiode array and a purpose-built probe head. The instrument is set to cover a spectral range from 1480 nm to 1950 nm. Spectra were measured in reflection or transflection mode using a ceramic back-reflector. The spectroscopic instrumentation is described in more detail in Reference 6.

Single spectra were taken continuously while the spot was scanned across the surface of the sample. After the scan, the accumulated spectra (about 1000) were averaged. For each sample, at least 10 average spectra were recorded. Quantitative analysis of the spectra was carried out on the basis of the partial least squares (PLS) algorithm.



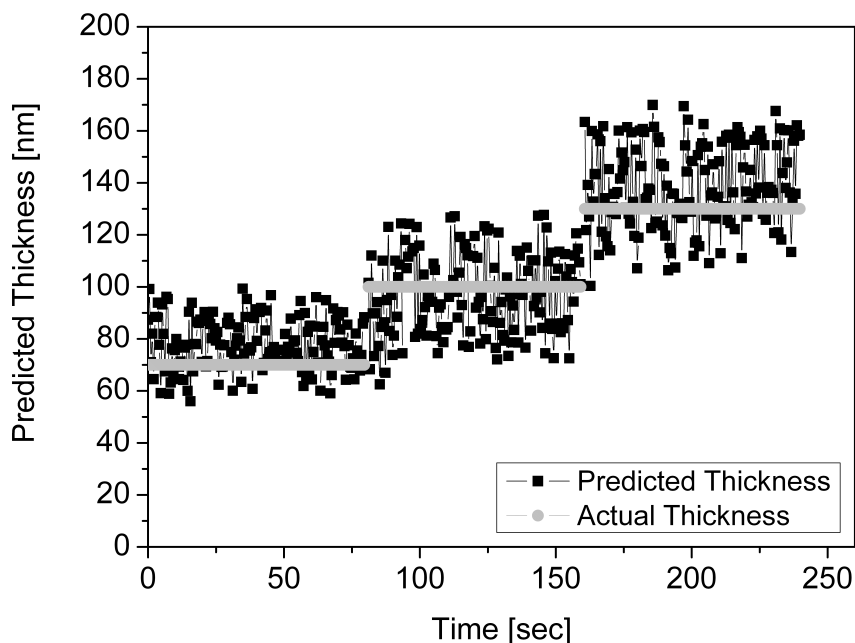
**Figure 3.** Prediction of the coating weight of independent test samples using the PLS calibration in Figure 2 and comparison with reference data from gravimetry.

## Results and discussion

Figure 1 shows NIR spectra of dried PHPS layers with different thicknesses on silicon wafers. It can be clearly seen that significant bands do not appear in the spectra (the band around 1910 nm originates from the wafer). Similarly, bands were not observed in the spectra of  $\text{SiO}_x$  layers, i.e. the spectrum strongly resembles that of PHPS. The lack of absorption bands might be due to the extremely low thickness of the samples (and in case of  $\text{SiO}_x$  also the lack of hydrogen-containing bonds). However, a slight variation in reflectance ( $\Delta R \approx 3\%$ ) was found, which is the basis for the quantitative determination of the thickness of the inorganic coatings by chemometric methods.

For calibration of the NIR spectra of silazane coatings on 23  $\mu\text{m}$  PET foil to the thickness, samples with different thicknesses were prepared and characterised by gravimetry. Data were converted into the thickness of the layers using the density of PHPS ( $\rho = 1.3 \text{ g cm}^{-3}$ ). When the PLS calibration model was built up, various kinds of pre-processing of the spectra were tested in order to optimise the calibration model. They were evaluated on the basis of the root mean square error of prediction (*RMSEP*) and the coefficient of determination  $R^2$ . Analysis of the total spectral range and simple normalization of the spectra proved to be the optimum method. The calibration function is given in Figure 2.

In order to check the capability of the PLS calibration model to predict the thickness of PHPS layers, further samples were prepared and analysed by use of this model. Figure 3 compares the results of the prediction from the NIR spectra with gravimetric reference data. The results clearly show that the thickness of inorganic layers in the submicron range can be determined by NIR spectroscopy with rather high precision.



**Figure 4.** In-line monitoring of the coating thickness of a silazane-based coating applied to PET foil. The actual thickness was calculated from the material flow through the calibrated slit nozzle.

For in-line monitoring, the NIR probe head was mounted above the web in the coating machine. Spectra based on 350 accumulations were recorded continuously, which resulted in a time resolution of 115 spectra min<sup>-1</sup>. Figure 4 shows the record of a typical in-line monitoring trial. In order to simulate changes of the thickness during a real coating process, the dosage of the PHPS solution was stepwise increased. It is evident that the resulting thickness changes in the order of 30 nm can be detected by NIR spectroscopy. The average thickness of the layers was also estimated from the material flow through the slit nozzle. Results are given as reference values in Figure 4.

The very close correlation between actual and predicted thickness clearly proves the suitability of the NIR method to predict the thickness of inorganic layers with a thickness in the submicrometer range from spectral data recorded during in-line monitoring trials. The maximum error can be estimated to be in the order of 20%.

The homogeneity of silica coatings across the coated web can be studied by use of this method as well, which has already been shown previously.<sup>7</sup>

## References

1. Y. Naganuma, S. Tanaka, C. Kato and T. Shindo, *J. Ceram. Soc. Jpn.* **112**, 599 (2004).
2. L. Prager, A. Dierdorf, H. Liebe, S. Naumov, S. Stojanović, R. Heller, L. Wennrich and M.R. Buchmeiser, *Chem. Eur. J.* **13**, 8522 (2007).
3. T. Scherzer, K. Heymann, G. Mirschel and M.R. Buchmeiser, *J. Near Infrared Spectrosc.* **16**, 165 (2008).
4. K. Heymann, G. Mirschel, T. Scherzer and M.R. Buchmeiser, *Vibr. Spectrosc.* **51**, 152 (2009).
5. L. Prager, L. Wennrich, R. Heller, W. Knolle, S. Naumov, A. Prager, D. Decker, H. Liebe and M.R. Buchmeiser, *Chem. Eur. J.* **15**, 675 (2009).
6. T. Scherzer, R. Mehnert and H. Lucht, *Macromol. Symp.* **205**, 151 (2004).
7. T. Scherzer, G. Mirschel, K. Heymann, L. Prager and M.R. Buchmeiser, *Appl. Spectrosc.* **63**, 239 (2009).