IR REFLECTOMETRIC INTERFERENCE SENSING APPROACH FOR GAS ANALYTES

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Introduction

Various optical methods have been exploited in chemical sensors including surface-plasmon resonance, ellipsometry, grating coupler, resonant mirror, Mach-Zehnder, fluorescence, IR absorption, as well as reflectometric interference spectroscopy (RIfS).

The two main features of a sensing device are sensitivity and specifity. The sensitivity is prescribed by the sensor modality and design, whereas the degree of specificity is dependent on the detailed nature of the chemical surface of the receptor part.

In the present work RIfS and mid IR absorption spectroscopy are employed as sensitive techniques, whereas the specifity of the sensor is assured in part by the polymer film receptor layer and in part by the infrared spectrum of the analyte.

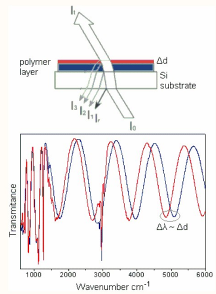

Figure 1. Schematic representation of the IR-RIfS method.

IR-RIfS method

In this set-up, one part of the IR radiation is reflected at the interface to the polymer layer, whereas the other penetrates the layer and is there reflected at the other interface. These two partial reflected beams become superimposed and due to the optical path difference, with increasing wavelength arise alternately destructive and constructive interference. The resulting interference pattern depends from the optical density of the polymer layer, which is given by the product of refractive index and physical thickness of the layer. Therefore, the interference spectrum enables the exact determination of the physical thickness of the layer, by knowing the refractive index of the polymer.

The extremes of the interference pattern are influenced either by swelling of the polymer film caused by permeation of gases, or by absorption of molecules into the layer. Therefore, the interference spectrum enables continuous monitoring of thickness changes of the polymer layer.

Thus, the obtained spectrum contains the IR absorption intensities of the polymer (and analytes) as well as the interference pattern, due to the thin polymer layer. The IR absorptions contain qualitative information (which analyte), whereas the interferogram part of the spectrum contains information about the thickness of the layer. The analyte concentration can be deduced by monitoring the swelling of the polymer layer, due to analyte absorption, as usually applied in reflectometric interference spectroscopy (RIfS). Hence, this set-up has the main advantage of no need of IR absorption intensities calibration for achieving quantitative information.

Coating materials and procedures

5-10% polymer dilutions were spin coated for 90 seconds at 2000 rpm on Si plates by using an spin coater (Convac 2001, Wiernsheim, Germany). The sensitive layer thickness was also determined by a surface profilmeter (Alpha Step 500, Tencor Instruments, Mountain View, USA).

The gas analytes were generated using a gas mixing station with computer-driven mass-flow controllers (MKS, Munich, Germany). A four-way valve before the cell ensured that the path length was the same for all analytes. Dry synthetic air was used as carrier gas. All measurements were performed at a constant flow rate of 300 ml min^{-1}.

FTIR-RIfS spectra with resolution of 4 cm^{-1} were obtained by using Bruker Equinox 55 and IFS 66 spectrometers equipped with liquid nitrogen cooled mercury-cadmium-telluride detectors.

Figure 2. Different set-ups for IR-RIfS spectra recording

Results and discussion

The molecular specific IR absorption and the corresponding interference spectra due to the Makrolon (M), Polyuretan (PUT) and Polydimetylsiloxane (PDMS) polymer films coated on Si plates, were obtained by using the IR-RIfS method, as showed in Figure 3. The main IR absorption bands of the corresponding polymers arrise in the 500-1700 and 2800-3400 cm^{-1} region, whereas in the range above 2000 cm^{-1} arise the interference spectra due to the thin polymer layer.

The thicknesess of the polymer films were calculated from the interfernce spectra Also, the film thicknesses were estimated with an alphastepper and the SD was found to be below 10%.

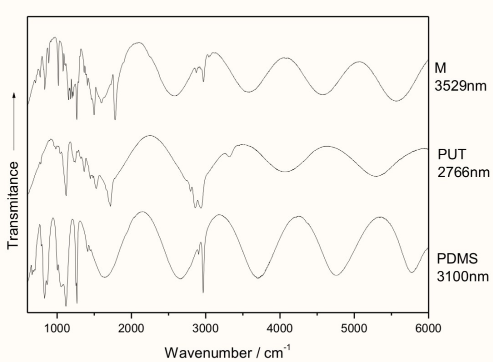

Figure 3. IR and interference (IR-RIfS) spectra of Makrolon (M), Polyuretan (PUT) and Polydimetylsiloxane (PDMS) as well as the calculated film thickness.

A 3 µm PDMS polymer coated on a Si plate was chosed as model substrate and the swelling by different analytes was monitored. Figure 4 shows the IR spectra and the interference patterns of the PDMS polymer exposed to the analyte gases toluene, m-xylene and dichlorbenzene.

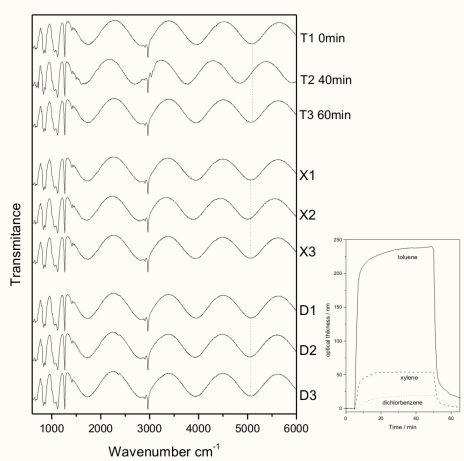

Figure 4. Swelling of a 3µm PDMS polymer under the influence of 6200 ppm toluene (T), m-xylene (X) and dichlorbenzene (D). Adsorption and desorption of the analyte gases in the PDMS layer in time.

The spectra of the gas analytes can be clearly evidenced by spectra subtraction, as shown in Figure 5.

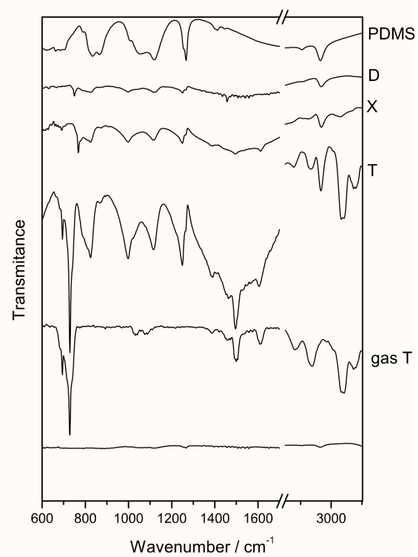

Figure 5. Top of the figure, the IR spectrum of a 3µm PDMS polymer layer. Difference spectra: D=D2-D1 (notation from Fig.4), X=X2-X1, T=T2-T1. The IR spectrum of toluene gas, (gas T). Bottom, the difference spectrum T3-T1.

Conclusions

The described IR-RIfS sensory technique represents a very efficient method for gas monitoring in terms of sensitivity and selectivity.

The molecular specific IR absorption enables high selectivity, leading to qualitative information.

The RIfS interference pattern enables the monitoring of the polymer layer thickness and by knowing the polymer physical properties, quantitative information can be achieved.

References

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