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In-situ characterization of thin polymer films for applications in chemical sensing of volatile organic compounds by spectroscopic ellipsometry

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Abstract Polymer coatings are applied in many kinds of chemical sensors. The interaction with organic vapours changes the physical properties of the coating material. For optical sensors, changes in the coating volume and the complex refractive index are most important. Spectroscopic ellipsometry has been applied for the first time to the in-situ characterization of thin poly(dimethylsiloxane) films in contact with tetrachloroethene, toluene and cyclohexane vapours. The differences in bulk refractive index between organic solvent and polymer are large for toluene and tetrachloroethene and both effects were studied separately. Cyclohexane has a bulk refractive index very close to the investigated poly(dimethylsiloxane) films. Therefore the calculation of the volume fraction of the analyte in the mixture phase with the polymer is subject to large errors for vapour concentrations below 5000 ppm.

1 Introduction

Polymers are important materials for the analysis of organic compounds. Well-known applications are stationary phases for gas chromatographic separation of complex mixtures of organics and solid phase microextraction for bulk enrichment of traces of analytes. During the recent years, special classes of polymers have been applied to chemical sensors as sensitive coatings for volatile organic compounds (VOCs). Much work has been done on coating materials for resonant transducers like bulk acoustic wave devices (e.g. [1]), surface acoustic wave devices

(e.g. [2]), and fibre optical or integrated optical transducers (e.g. [3, 4]). In all these cases, the sensor effect arises from a fast and reversible enrichment of organic compounds by thin films of polymers which changes the physical properties of the coating. Steady state monitoring of changes in density or viscosity by mass sensitive transducers, dielectric constant by capacitive transducers, and thickness and complex refractive index by optical transducers is common as well as monitoring the transient temperature changes that arise from the heat of absorption with thermopiles. The affinity of polymers towards organic molecules is described by the thermodynamic coefficient of distribution [2]. The interaction is based on relatively weak dispersion forces and the partial sensitivity may be attributed to molecular parameters and predicted by linear solvation energy relationships [5]. Many groups have demonstrated that tailored arrays of sensors coated with different materials may be used to discriminate and quantify fairly complex mixtures of organic solvent vapours. Recently, we presented applications in water analysis [6].

Coefficients of distribution may be estimated assuming ideal mixing of polymer and analyte from the mass increase of quartz resonators and compared to data from gas chromatography. However, the increase in mass monitored by the frequency shift of acoustic devices is accompanied by an increase in volume and the increase in volume monitored by optical interferometric transducers is accompanied by a change in the coating refractive index that is due to the mixing of polymer with analyte. The change in refractive index comprises valuable information about the volume fractions of analyte and polymer molecules in the resulting mixture phase and therefore about its composition. For a full understanding of the polymer/analyte interaction, it is therefore essential to study all contributions to the overall change separately.

In this paper, we describe experiments for the in-situ characterization of polymer coatings in contact with VOC vapours. The goal is to separate changes in volume caused by swelling of the polymer film and changes in refractive index caused mainly by mixing with the analyte. Re-

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cently, white light interferometry at thin non-absorbing polymer films has been described for the separation of both effects [7]. Volume increase and refractive index changes were monitored, combined in the optical thickness of thin polymer films, by an optical transducer based on the reflectometric interference spectrometry (RIFS). However, only relative data are available by this technique. In this work, we investigated the applicability of spectroscopic ellipsometry for obtaining absolute values. Coatings of a standard poly(dimethylsiloxane) were characterized. We selected a stationary phase from GC as (i) a basic model system for many standard side chain modified poly(siloxanes) and (ii) as a basis for further work, where specific selector molecules will be covalently linked to the siloxane backbone in varying concentrations. As model analytes for typical hydrocarbon solvents, we used tetrachloroethene, toluene and cyclohexane.

2 Spectroscopic ellipsometry

Spectroscopic ellipsometry [8] is usually used for the analysis of thin films, bulk materials and surfaces. The advantage of this technique is that it is a non-disturbant optical method. With ellipsometric measurements one determines the two ellipsometric angles $\tan \Psi$ and $\cos \Delta$. These angles describe the change of the state of polarization of the incident beam due to the reflection at the probe interfaces. The product ρ of the two ellipsometric angles is defined as the ratio of the complex coefficients of reflection of parallel and perpendicular polarized light relative to the plane of incidence:

$$\rho = \tan \Psi \cdot e^{i\Delta} = \frac{R_p}{R_s} \quad (1)$$

These coefficients depend on the layer structure and it is possible to separate the thickness of a thin film and its refractive index if the optical properties of the substrate and the ambient are known. The explicit dependence for a single layer between a substrate and an ambient medium is included in the appendix. Small changes in thickness (< 2 nm) and refractive index (< 0.005) can be easily detected. The interaction of the studied polymer films with solvent vapours is considerably fast with typical coefficients of diffusion within the range of 10^{-12} m²/s to 10^{-11} m²/s at room temperature and fully reversible within a few seconds. The permeation of analyte molecules into the polymer film leads to an increase of film thickness and a change of refractive index. The resulting refractive index of the polymer/analyte mixture phase can be higher or lower than the initial refractive index, depending on the refractive index of the analyte. To describe the dispersion of the refractive index of the pure polymer, we used the Cauchy parametrization model [9]. This parametrization (Eq. 2) neglects the imaginary part of the refractive index and is justified because the measurements were carried out in the wavelength range of 300 nm to 800 nm where the studied films are non-absorbing.

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \quad (2)$$

From the mixture refractive index of the swollen polymer, the volume fraction of the analyte in the binary mixture can be obtained using a Bruggemann effective medium approximation [10]:

$$\Phi \frac{n_a^2 - n^2}{n_a^2 + 2n^2} + (1 - \Phi) \frac{n_p^2 - n^2}{n_p^2 + 2n^2} = 0 \quad (3)$$

Φ corresponds to the volume fraction of the analyte in the binary mixture, n_a is the refractive index of the pure analyte phase, n_p is the refractive index of the pure polymer phase, n is the refractive index of the resulting mixture phase.

3 Experimental

3.1 Set-up for in-situ characterization. For the measurements described in this paper, a scanning spectroscopic ellipsometer (SOPRA model ES4G, SOPRA, France) was used. The interaction of thin polymer films with solvent vapours was investigated using the in-situ set-up depicted in Fig. 1. Analyte vapours with defined partial pressures were generated from cooled bubblers filled with pure liquid analytes using synthetic air (20% O₂ and 80% N₂, Messer Griesheim, Germany) as carrier gas and then diluted to known concentrations by computer-driven mass flow controllers (MKS, Munich, Germany). All vapours were thermostated before entering the cell. The gas generator allows the reproducible preparation of concentrations within the range of some ppm and a few thousand ppm. The time for one measurement was approx. 2 h. All measurements were done with an angle of incidence of 73° within the range from 300 nm to 800 nm and replicated. The standard deviation is indicated by the error bars in the figures. The data analysis is done with software developed in our group.

3.2 Preparation of poly(dimethylsiloxane) films. For this study, we used a commercially available poly(dimethylsiloxane) stationary phase (PDMS) from gas chromatography (ABCR Karlsruhe, Germany). The average molecular weight was 30 000 g/mol. The siloxane chains are not cross-linked. For the measurements, films of approximately 1 μm were prepared by spin coating dilute solutions of PDMS in toluene (HPLC grade, Aldrich) at 7000 rpm on flat silica (253.9 nm) on silicon substrates (2 cm × 2 cm, Wacker Chemie, Burghausen, Germany).

For cleaning, the substrates were first treated with tetrachloroethene (analytical grade, Merck Germany). In a second step the surface was treated for half an hour with piranha solution (30% Vol. H₂O₂ (30%) and 70% Vol. concentrated H₂SO₄) followed by

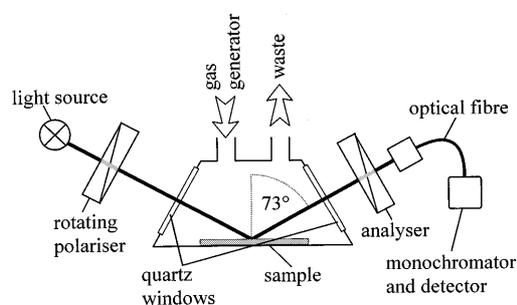


Fig. 1 Schematic set-up for the ellipsometrical in-situ characterization of the changes in thickness and refractive index of thin polymer films in contact with organic vapours

Table 1 Refractive indices of toluene, tetrachloroethene and cyclohexane according to [11]

Wavelength [nm]	Toluene (15°C)	Tetrachloroethene (20°C)	Cyclohexane (20°C)
656.2	1.4951	1.50153 1.5014	1.42476
589.6	1.49985	1.50547 1.5053 1.5055	1.4266 1.42622 1.4264
587.6			1.4268
486.8	1.51134		1.43229
434.0	1.52139	1.52368	1.43668

Table 2 Cauchy parameters calculated from the literature data in Table 1

Parameter	Toluene	Tetrachloroethene	Cyclohexane
A	1.47704	1.48599	1.4171
B [nm ²]	7345.13	6318.63	2797.1
C [nm ⁴]	1.89×10^8	1.47×10^8	1.72×10^8

rinsing with deionized water. Finally, the substrates were cleaned with HCl (half concentrated, analytical grade, Merck Germany), rinsed with deionized water, and dried in vacuum at 80°C for 1 h. After that the films are prepared by spin coating in a class 1000 clean room. To remove the solvent, the films were kept for at least 2 h in vacuum at 60°C.

3.3 Refractive indices. The evaluation of ellipsometric data was based on refractive index data found in the literature [11] for toluene, tetrachloroethene and cyclohexane. The values for different wavelengths are listed in Table 1. With these values a Cauchy parametrization was done for the refractive index of the analytes. The parameter values obtained are shown in Table 2.

4 Results and discussion

The films prepared according to the procedure described in the experimental section were inserted in the measurement chamber and subjected to measurements in atmospheres of dry synthetic air and synthetic air enriched with analytes. The vapour concentrations (partial pressures) were in the range from 340 ppm (34.5 Pa) to 8500 ppm (862 Pa) for toluene, 200 ppm (20.4 Pa) to 5000 ppm (509 Pa) for tetrachloroethene, and 1100 ppm (121 Pa) to 28000 ppm (3.02 kPa) for cyclohexane. The ellipsometric angles for a 924 nm film in dry air are indicated by the solid lines in Fig. 2a, b. The dotted lines correspond to the data fitted with the layer model shown in Fig. 2c. The deviation in the peaks of $\tan \Psi$ and $\cos \Delta$ is due to inhomogeneities of the film thickness. These differences can be described by a model including a non-uniform surface. In this model [12] the probed area is divided into smaller subareas each with uniform thicknesses. As result, an average film thickness is obtained and an additional parameter characterizing the width of the thickness distribution. The results show good correspondence with the measurements and the mean thickness is in agreement with the results obtained with a model of uniform film thickness

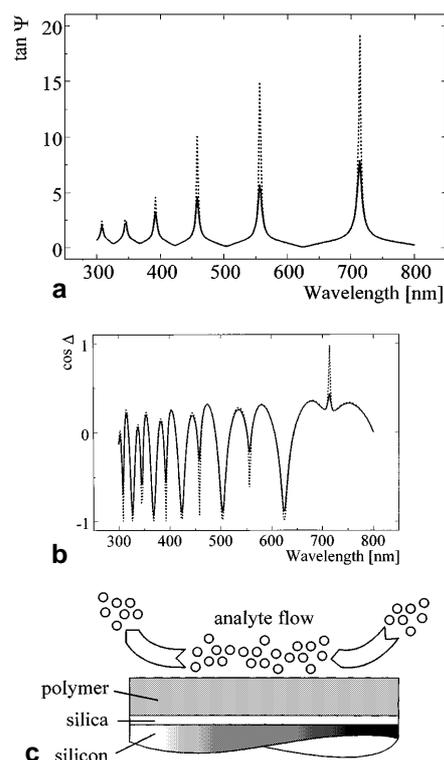


Fig. 2a, b Ellipsometric angles versus wavelength for a PDMS film on a thermally oxidized silicon wafer in contact with dry air: **a** $\tan \Psi$; **b** $\cos \Delta$. The *solid lines* indicate the measured data. The *dotted lines* represent the data obtained from the layer model in **c**. Details are given in the text

(923.76 nm). The inhomogeneity is estimated to 1% of the average thickness. Since no technique was available to verify the film inhomogeneity, the data evaluation was furtheron based on the homogeneous system given in Fig. 2c. Further investigations will be conducted to include and reference inhomogeneities. The Cauchy parameters obtained for PDMS are:

$$A = 1.4076 \pm 7.5 \cdot 10^{-7}, B = 2850.3 \pm 0.33 \text{ nm}^2, \\ C = 1.3416 \cdot 10^8 \pm 2.9 \cdot 10^4 \text{ nm}^4.$$

Figure 3a demonstrates the increase in film thickness for different concentrations of the analytes. The concentration range up to 6000 ppm is zoomed in Fig. 3b. No significant deviation from linearity was detectable for toluene and tetrachloroethene on a 95% confidence level. The sensitivity towards toluene is lower by a factor of 1.69 than towards tetrachloroethene. For cyclohexane, the increase in thickness is linear for concentrations higher than 5000 ppm. For lower concentrations the data imply a strong deviation from linearity (cf. Fig. 3b). The reason for this is obvious from an inspection of the corresponding refractive index of the swollen polymer phase (Fig. 4). The figure shows the film refractive index at 589.6 nm (n_D) and 20°C calculated from the ellipsometric angles in dependence on the vapour concentration. The bulk refractive index of all analytes is higher than the bulk refractive index of the polymer. Consequently, the refractive index of the

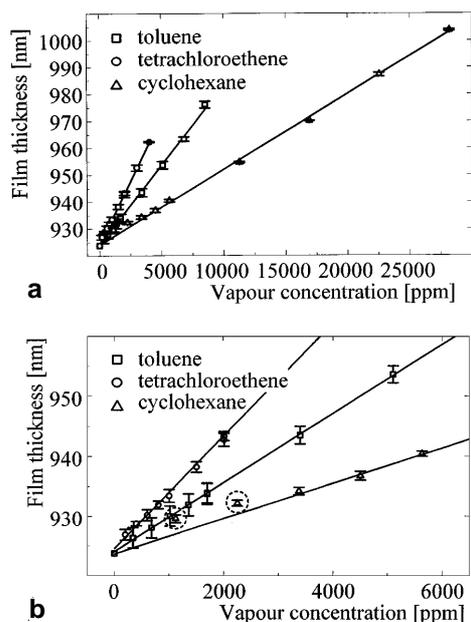


Fig. 3 **a** Change of the thickness of a PDMS film versus analyte concentration. **b** Zoomed portion of **a** for the concentration range up to 6000 ppm

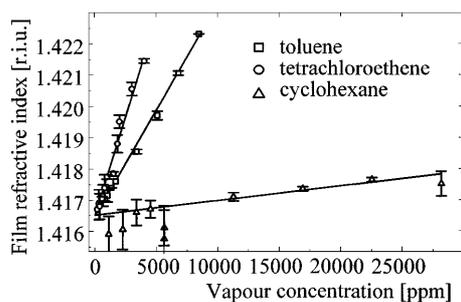


Fig. 4 Refractive index of the resulting mixture phase *PDMS*/toluene, *PDMS*/tetrachloroethene, and *PDMS*/cyclohexane at 589.6 nm and 20°C versus analyte concentration

polymer coating increases with increasing analyte fraction. For toluene and tetrachloroethene, the bulk refractive index differences are 8.335×10^{-2} and 8.897×10^{-2} , respectively. The bulk refractive index difference for cyclohexane is lower by one order of magnitude (9.9×10^{-3}). In addition, it is known from earlier investigations, that cyclohexane has a much lower affinity for PDMS than toluene or tetrachloroethene, as is indicated by the coefficients of distribution [13]. Therefore we expect a very small change in refractive index at concentrations below 5000 ppm and the intrinsic correlation between thickness and refractive index during the data evaluation step (non-linear regression) dominates the results. The large error bars for cyclohexane below 500 ppm in Fig. 4 reflect this fact. A comparison of Figs. 3b and 4 shows that the refractive index is estimated smaller than it would be expected from the data obtained for higher concentrations and the corresponding film thickness is estimated too high with the consequence that the data fitted for cyclohexane

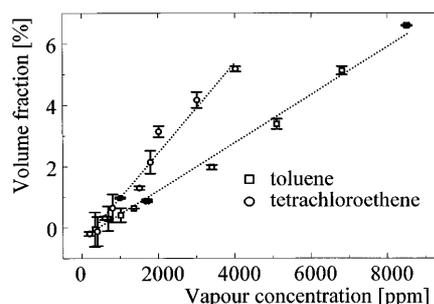


Fig. 5 Volume fraction of toluene and tetrachloroethene in the polymer film, depending on the vapour concentration

within this concentration range are not reliable. We expect that data evaluation and the quality of the fitted data can be improved by (i) preparation of more homogeneous films and (ii) taking film inhomogeneities into account. Currently, we are working on both topics.

The volume fraction of analyte in the mixture phase, that has been calculated on the basis of the Bruggemann model (Eq. 3), is presented in Fig. 5 for toluene and tetrachloroethene.

5 Conclusion

Changes in volume and refractive index induced by the interaction of organic solvent vapours with polymer films may be quantified separately by spectroscopic ellipsometry. The results obtained with the model system are encouraging. The results demonstrate the potential of the ellipsometric technique for in-situ characterization of bulk interactions. Further studies will be conducted (i) to compare the ellipsometric data with data from interferometric measurements where refractive index and volume increase have been deconvoluted according to work reported recently in this journal [7], (ii) to study the interaction of organic molecules with supramolecular selectors that are covalently linked to the polymer backbone in varying concentration, and (iii) to examine the analysis of inhomogeneous films.

Appendix

Dependence of the ellipsometric angles on the film thickness and refractive index

In case the system under consideration only includes a single interface between two isotropic media, the complex coefficient of reflection R_S and R_P depends on the angle of incidence Φ_0 of the incoming beam, the refractive index of the ambient n_0 and of the substrate n_1 and on the angle Φ_1 of the refracted beam according to equations (4) and (5):

$$R_S = r_S = \frac{n_0 \cdot \cos \Phi_0 - n_1 \cdot \cos \Phi_1}{n_0 \cdot \cos \Phi_0 + n_1 \cdot \cos \Phi_1} \quad (4)$$

$$R_P = r_P = \frac{n_1 \cdot \cos \Phi_0 - n_0 \cdot \cos \Phi_1}{n_0 \cdot \cos \Phi_1 + n_1 \cdot \cos \Phi_0} \quad (5)$$

In this case R_S and R_P are equal to the Fresnel coefficients of reflection r_S and r_P for parallel (index p) and perpendicular (index s) polarized light.

For a multilayer system the theoretical description is more complicated. The coefficients of reflection and their ratio are functions of the refractive index of all layers, the angle of incidence, and the thicknesses of the layers. The analytical solution for a single layer (subscript 1) deposited on a substrate (subscript 0) and surrounded by an ambient medium (subscript 2) is given by Eq. (6).

$$R_S = \frac{r_{01S} + r_{12S} \cdot e^{-i2\beta}}{1 + r_{01S} \cdot r_{12S} \cdot e^{-i2\beta}} \quad (6)$$

$$R_P = \frac{r_{01P} + r_{12P} \cdot e^{-i2\beta}}{1 + r_{01P} \cdot r_{12P} \cdot e^{-i2\beta}} \quad (7)$$

In Eq. (6), r_{01S} , r_{01P} , r_{12S} and r_{12P} correspond to the Fresnel coefficients of reflection (4), (5) on the interfaces between the ambient and the layer and between the layer and the substrate. The phase shift β or layer phase thickness is given by:

$$\beta = \frac{2 \cdot \pi \cdot d_1 \cdot n_1}{\lambda} \cdot \cos \Phi_1 \quad (8)$$

where d_1 is the thickness of the layer and n_1 is the dispersion of the layer. Φ_1 is the angle between the direction of propagation of the light wave in the film and the normal to the film boundaries.

For two and more layers, the calculation can be done by matrix calculations or recursive calculation according to [8]. The reverse calculation of the thickness and the refractive index from the ellipsometric angles may be carried out by standard non-linear regression algorithms.

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