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Sol-gel protective layer for fiberoptic chemical microsensors

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The sol-gel-derived materials can be used in construction of various optoelectronic devices, including optodes of fiberoptic sensors. The porous matrices provide excellent media for a variety of organic and inorganic compounds, which can serve as detectors. They can work in various environments with different refractive indices. In this study, we report on the influence of the refractive index of external media on the overall performance of the fiberoptic chemical microsensors. Especially, the sensors based on the intensity measurement are influenced by the refractive index of environment. The application of the sol-gel thin film as a protective layer of microoptode is discussed. The light intensity angular distribution was examined for both bare fiber tip, as well as for the tip covered with a sol-gel layer. The magnitude of microsensor response signal was measured, as well. The smaller signal decrease was observed for microoptode covered by sol-gel. A possible application of the method described for fiberoptic oxygen microsensor is discussed.

1. Introduction

Silica gels are used as matrices for entrapping different components for optical sensors. The preparation of this material is broadly discussed in the literature [1]. The features of silica gels connected with transparency and porosity facilitate transport of gases through the material. Their thermal and chemical stability and ability to be filled with additional active phases are the key properties exploited for sensor applications [2].

Quite a new field of sol-gel application is the microscale optics for chemical sensing, which was first reported in 1996 [3]. The preparation of organically doped room temperature processed sol-gel-derived microscale optical waveguides as platforms for chemical sensors and biosensors was presented. A number of interesting applications have been proposed for sol-gel microoptics [4]–[6]. In this work, we report on the application of the sol-gel thin films for protection of fiberoptic micro-optodes.

2. Microoptodes

Whenever high spatial resolution measurements are needed the microsensors must be used. Microoptodes for fiberoptic chemical sensors are quite a new branch of

optical chemical sensing but they became already an interesting alternative for chemical microelectrodes. Optical microoptodes have a number of advantages over electrodes. Fiberoptic microoptodes offer high measuring range, low cross-sensitivity, long term operation and storage stability, and they are a low cost solution. In spite of the great advantages, there are always weak points. One of these is the mechanical stability of such microoptodes and its dependence on change of the refractive index in the surrounding media.

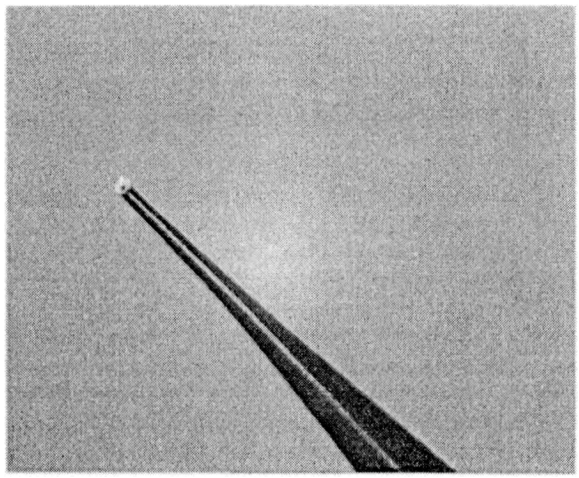

Fig. 1. Tapered fiber tip.

Microoptode has exactly the same function as normal optode, but it is prepared in microscale. A typical diameter of the optode is ca. 100 μm, whereas microoptode are smaller than 50 μm. This results in the high spatial measurement resolution and very fast response time (due to the tiny amount of active media) of the micro-optode based sensors. Such a fiber tip is presented in Fig. 1.

3. Experimental material

For the experiments, typical telecommunication optical waveguides were used (125/62.5 μm – from Radiall). Fiber tips were tapered in the shape of cones, so they were approximately 30 μm in diameter and 2 mm in length. In this study, the tapered fiber tip was prepared by means of hot torch method.

The precursor for the sol-gel thin films used in the experiment was TEOS (tetraethoxysilan 98% from Aldrich) stired with EtOH (ethyl alcohol) with addition of HCl as a catalyst. The material was prepared in the following proportions: 42 ml of ethyl alcohol, 5 ml of TEOS, 1.6 ml of Triton X-100 (Aldrich) and 1 drop of 36% HCl. Detergent Triton X-100 lessens the surface tension, thus making the sol-gel-to-substrate contact better. All these substances were mixed together by means of magnetic stirrer for 4 h at room temperature. The liquid sol-gel was used to cover the tapered fiber tip.

Compared to the conventional thin film forming, sol-gels are ideal for preparing thin films in such simple processses as diping, spinning or spraying. Formation of the thin layer requires considerably less equipment and makes it possible to control the microstructure of deposited film. In our experiment we used a dip-coating method. It is similar to the technique of dragging of the liquid by a moving plate described already in 1942 by LANDAU and LEVICH [7]. According to this work, the thickness of deposited film depends on liquid density and viscosity, surface tension, withdrawal speed of the substrate (in our case fiber tip).

The slower the fiber speed, the thinner the film and the greater the overlapping of deposition and drying stages. Since the condensation continues during sol-gel film formation, the relative condensation and evaporation rates will determine the extent of further cross-linking that accompanies the deposition and drainage stages. All types, the decladed, the unjacked, tapered or just cut fibers, can be covered by sol-gel by means of the dip-coating method. The sol-gel thin films prepared for this experiment were 0.5 μm thick.

4. Measurements

Two types of examinations were performed. First, angular distribution of the light intensity in the tapered tip with and without sol-gel protective coating was measured. Second, the oxygen sensor signal intensity was examined in both cases: for protected micro-optode and for the bare one. Schematic experimental set-ups are shown in Figs. 2 and 3, respectively. The protective sol-gel layer was practically tested using the commercially available oxygen microsensor (MICROX 1, from PreSens GmbH, Germany).

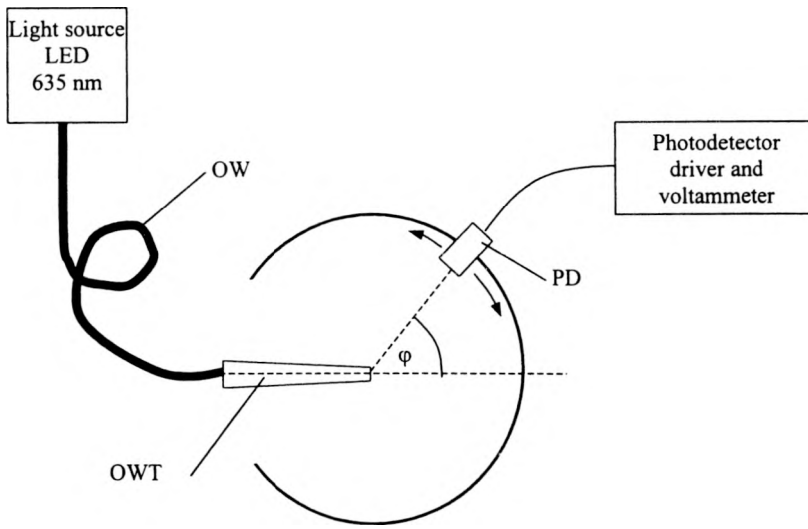

Fig. 2. Angular light intensity measuring set-up. PD – photodetector (photodiode), OW – optical waveguide (125 μm silica fiber), OWT – optical waveguide tip (magnification of the tapered fiber).

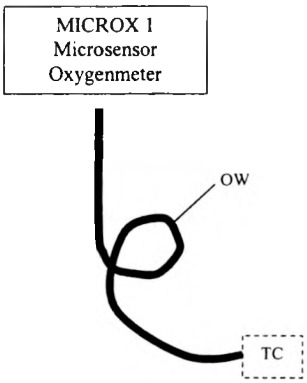

Fig. 3. Signal intensity measuring set-up for the oxygen microsensor. OW – optical waveguide (125 μm silica fiber) with the microsensor at the tip, TC – test chamber filled with water or air. MICROX 1 – fiberoptic oxygen meter used by courtesy of PreSens GmbH, Germany.

The angular intensity spectrum was examined in order to find out the influence of the tip coating on the light intensity distribution at the fiber end. As a light source the light emitting diode $\lambda = 635$ nm was used. The light was coupled to the optical fiber and guided to the fiber tip with attached optode. The photodetector was placed on a rotating arm at a distance of 1 cm from the fiber end and connected to the voltameter. The signal was collected stepwise every 1.8°.

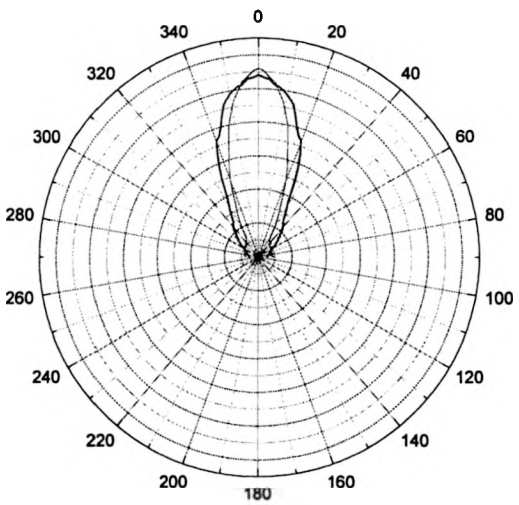

Fig. 4. Angular light intensity distribution for coated (bold line) and uncoated (thin line) fiber tips.

The results obtained are shown on the polar plot depicted in Fig. 4. The bold line represents the light intensity distribution around the tapered fiber tip coated with the sol-gel thin film. The thin one stands for the uncoated tip. It is seen that the presence of the thin sol-gel layer significantly influences the light distribution around the tip. Practically, no light is seen at the angle over 30 degrees in the case

of uncoated fiber, whereas there is still light emitted from the covered tip at the angle of 45° . However, in the last case the lower signal is observed at the angle 0°, mainly due to the scattering in the sol-gel film.

The effect demonstrated above indicates that in the case of coated fiber tip, more light can also be coupled to the fiber. Such light distribution leads also to more effective excitation of sensitive particles that are embedded in the sol-gel matrix, building the detecting part of an optode.

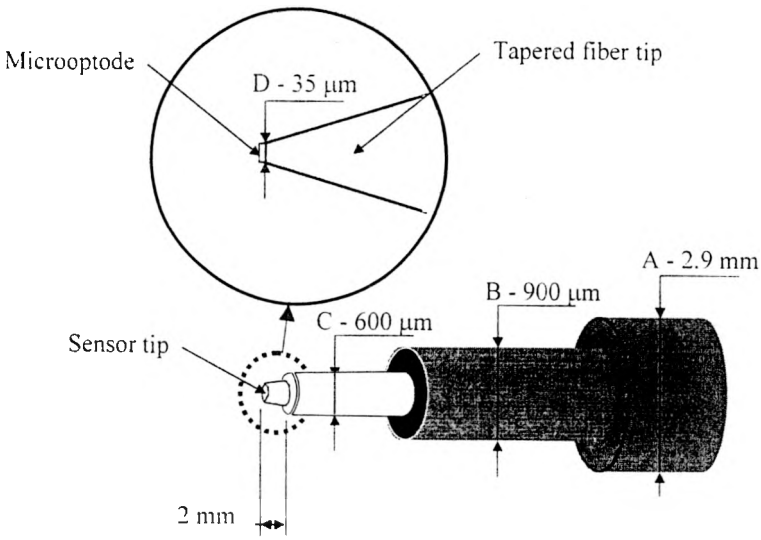

Fig. 5. Schematic drawing of the oxygen sensitive microsensor (PreSens GmbH, Germany). A – protective outer vinyl jacket, B – inner protective jacket, C – polymer shield over 125 μm silica fiber, D – diameter of the microsensor tip.

In the second part of the experiment, the commercially available oxygen microsensor was used. Its construction is schematically shown in Fig. 5. This microsensor is a Ruthenium complex based detector with the sol-gel optode attached to the tapered optical fiber. Sol-gel optode is a highly permeable matrix. The response time is below a few seconds. The sensor tip is a very fragile part and must be handled with care. Even during standard measurements the insertion of the probe into the test media causes sometimes the sensing material to chip off the fiber tip.

In our experiment, an additional sol-gel thin film layer prepared as already presented, covered the oxygen microsensor tip. The signals received from

Table. Changes in microsensor response signal dependent on the environment.

	Air signal [mV]	H_2O signal [mV]	Relative signal decrease [%]	Response time [s] (signal change from 0 to 100 %)
Uncovered	1089	504	53.72	3
Covered tip	850	490	42.35	3

covered and uncovered sensors are compared in the Table. The measurements were performed in air and in water. In both cases the same oxygen saturation in the test chamber was ensured.

Analysing the data from the Table, one can notice that signal amplitude changes when changing the environment from air to water. Over a 50% relative signal change for microsensor without any additional protective layer was observed. This clearly demonstrates that amplitude/intensity based measurements by means of optical chermical sensors are strongly environment dependent. (The MICROX 1 fiberoptic oxygen detector use here is free of this dependence because it relies on phase measurement principle). However, these results demonstrates that by applying the fiber tips covered with the thin sol-gel film, the improvement of the performance of amplitude microsensors can be achieved.

5. Conclusions

The application of sol-gel protective thin film layer for improving the performance of fiber optics microsensors was investigated. The signal amplitude reduction in the case of covered tips was observed, but the sol-gel protective layer had no influence on the sensor response time. The sensor signal changed due to the refractive index change in the surrounding environment. The relative change was more significant for uncovered sensor tip (53.72%) than for the covered one (42.35%).

Analysing the angular distribution of light emitted from both types of the fibertips, one can see that the protective sol-gel layer increases the light beam diameter. These results are important for construction of fiberoptic microsensors.

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