A low temperature operated NO_2 gas POF sensor based on conducting graft polymer

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Abstract—A simple POF sensor has been developed, which is used to detect and measure the concentration of nitrogen dioxide, at low temperatures (about 50°C). In this work, we present a thermal profiling process of the sensor head type POF, and the application of a sensing structure based on grafted polymer preparation by a dip-coating technique. We made characterization prepared structures and tests with various NO_2 concentrations at low temperature and dry atmosphere.

This work focuses on optical detection and optical measurement of low concentration nitrogen dioxides in low temperatures (about 50°C). Our sensing system for optical detection of NO_2 is based on a combination of plastic optical fiber (POF) and innovation sensing organic materials which are grafted polymers. Specially prepared sensor heads based on a POF type fiber optic are coated with a functionalized polymer by a dip-coating technique. This platform provides minimalizing costs of an elementary sensing point with relative stable sensing properties.

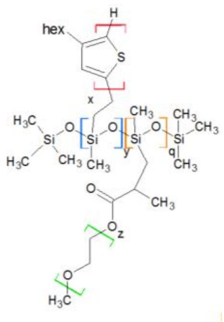

Fig. 1. The poly(siloxane)macromolecule grafted with p-doped P3HT and poly(ether) side chains.

Nitrogen dioxide is a strongly poisonous gas and it is produced, among others, at the production of nitrogen acid, sulfuric acid, fertilizers, during the explosion of some explosives, in the steel industry, chemical synthesis as an industry reagent and the combustion of fossil fuels (heating systems, inner combustion engines).

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Sensors based on semiconductor oxides are generally low in cost and show high stability [1-2]. At present, the market offers sensors enabling to measure and detect NO_2 in relative high temperatures and concentrations in ppm levels [2]. It is related with using semiconductor oxides as receptors because for them chemisorption takes place at relatively high temperatures (hundreds of Celsius degree). Therefore, it would be necessary to develop and fabricate practical, small, and low-cost sensor devices that can detect low NO_2 concentrations. This leads to the search for new materials, provides considerable growing sensitivity, speed and accuracy of measure.

Graft copolymers belong to a class of novel materials of segmented copolymers and generally consist of a linear backbone of one composition and randomly distributed branches of a different composition. The polysiloxane scaffold is well-known for its self-organization, taking place both between individual polymer chains and between polymer chains and substrate materials [3]. Such effects are known to occur, even for molecules in which the siloxane moieties are but a fraction of the actual polymer chain [3]. The use of the siloxane material attributes will afford covalently molecularly ordered π-conjugated materials, by combining the advantages of new materials with techniques of shaping the morphology of the organic layers. However, no less important issue is the use of functional siloxane scaffolds for the preparation of materials specifically targeted at a selected application – for specific gases. Usually, slight changes in the environment are sufficient to induce a greater change in the polymer properties. Polymetylosiloksane-graft-poly-3-(heksyltiophene)–graft-polyether material was obtained, according the scheme in Fig. 1. Its synthesis is described in detail in the patent [4].

A diagram of the experimental setup is shown in Fig. 2, consisting of a wide band light source (low power consumption halogen lamp), detector (spectrometer HR2000+ES, Ocean Optics), POF splitter with optical power distribution 30/70 (light source arm/detection arm),

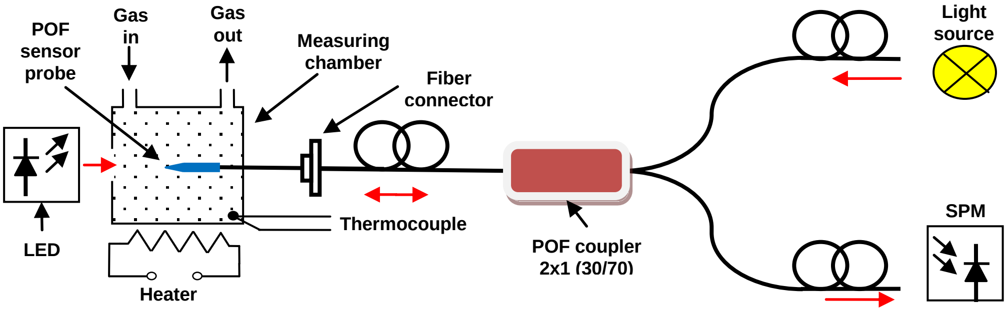

Fig. 2. Scheme of the optical experimental setup.

fiber optic FC type connector (for connecting POF sensing element), flow gas chamber with heater and temperature control (inside placed POF sensor head), and LED diode (λ=460nm directed on sensor probe). The POF sensor probe is connected to the system by an FC/FC connector using liquid index-matching. All kinds of optical fiber (lead-in fiber, 30/70 coupler, sensor probe) are with the similar outside diameter, which is in the order of 980/1000µm (Eska Premier GH4001, Mitsubishi Rayon). Light is partially reflected by the sensor head of the POF fiber coated with the poly(siloxane) grafted with p-doped P3HT and poly(ether) side chains film.

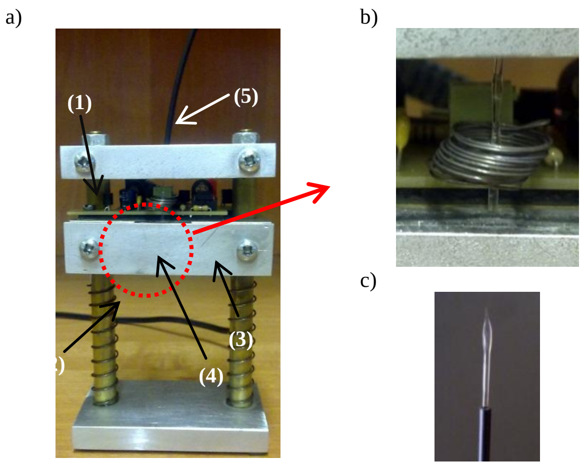

Fig. 3. Picture (a) of the device for thermal profiling POF type probes, (1) – top mount, (2) – weight, (3) – heater driver, (4) – heater, (5) – fiber optic (POF), (b) under profiling measuring head, (c) result of thermoforming.

The idea of measurements was to obtain the spectral reflection characteristics when exposed to a mixture of synthetic air with a varying content of NO_2 gas. Determined reflectance (reflected optical signal) is carrying information about changes taking place on a sensor structure, as a result of NO_2 adsorption.

The POF sensor heads were designed in order to increase the surface of a reaction sensor layer with a specific gas analit and light beam. Therefore fiber optic forehead with is measuring head, form for getting conical surface. The ends of a POF were thermoformed. The easiest way is to locally heat POF at a temperature of about 70°C and stretch it. To carry out this task, we used the device shown in Fig. 3a. It contains: top mount (1), movable weight (2), heater driver (3) and heater (4). Step-index POF 980/1000µm (5) is installed between the top mount (1) and movable weight (2), next it is heated by the heater (4). In consequence, gravity force results in falling weight (2) and enables to profile the fiber optic for a designed shape (Fig. 3c). Figure 3b shows the fiber optic at the moment of profiling.

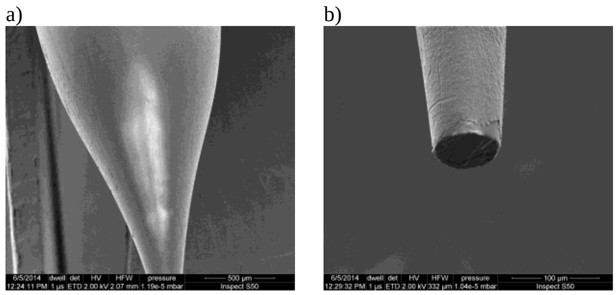

Fig. 4. SEM images of the POF type sensor head after thermoforming (a) view of the lateral surface of a fiber optic head, (b) view of the end of the head.

Thermoformed POF probes were observed with a scanning electron microscope (SEM). As shown in Fig. 4a, as a result of thermoformation, on the lateral surface of POF heads are formed micro cracks, probably caused by rapid heating and cooling of the fiber optic. Figure 4b shows the end of a head sensor. This shape is caused by fiber rupture in the last stage of thermoforming. In addition, we can observe that, as a result of thermoforming, fiber cladding is stretched for all lateral surface of POF heads.

The results of a thermoforming process indicate this method of profiling a sensor head has the repeatability of reflectance in a range of 15% from the average value. Figure 5 shows typical reflectance spectra of profiled POF probe and light beam spectra of halogen lamp transmitted via 15cm POF patch cord (GH4001).

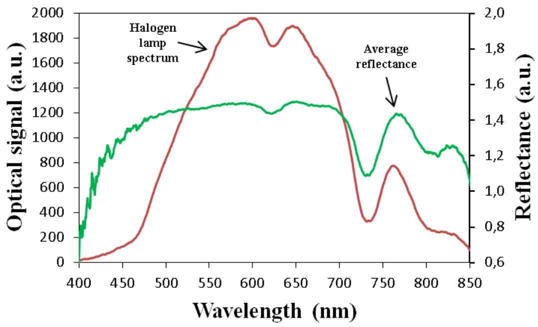

Fig. 5. Typical measured reflectance spectrum of POF probe and light beam spectrum emitted by halogen lamp via POF fiber.

Grafted polymer was dissolved in chloroform. The sensing structures were prepared by a dip-coating technique from the liquid phase. After the coating process, the coated POF probes were dried for 15min at 30°C. After solvents evaporation, the interfacial thin film resulted in a grafted polymer about several hundred nanometers thick. Fabricated sensor structures were studied by an SEM technique. As shown in Fig. 6, sensing thin film of a probe is not always regular (Fig. 6a) but it is so where the structure adheres well to POF in the presence of a highly develop surface. POF-based sensor heads were exposed to varying concentrations of nitrogen dioxide in a range from 0 to 10ppm in synthetic air, at 50°C and relative humidity of about 6% at RT.

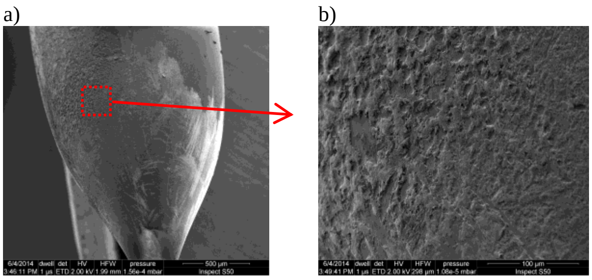

Fig. 6. SEM images of the POF type sensor head coated with a grafted conducting polymer (a) view of the lateral surface of the head, (b) morphology of the sensing structure.

Figure 7 shows preliminary measurement results of our sensor. In general, the variations in the reflectance between 750nm and 770nm can be used to discriminate concentrations of nitrogen dioxide in synthetic air. Structures exhibit strongly reaction to NO_2. The reproducibility in the adsorption and desorption processes of the gas was satisfactory. The reproducibility of NO_2 response as a function of time showed a decrease of the signal; which decreases in the next cycles of exposition. It suggested the degradation of sensing properties as a result of interaction with oxidizing gases. After several cycles, the sensitivity values tended towards stabilization but those sensors still require future research on modification of organic structures based on this type of grafted polymer.

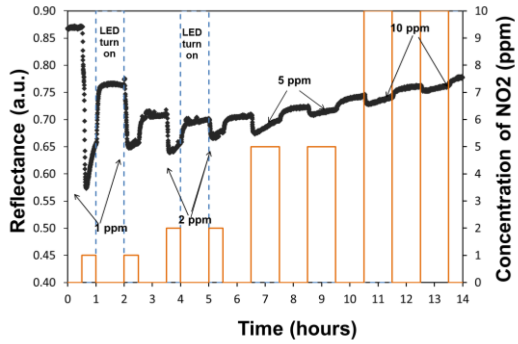

Fig. 7. The reflected optical signal (λ=760nm) variation of the POF based sensor versus time exposition to varying concentrations of NO_2 at a temperature of 50°C and dry air; dashed line – turn on LED (λ=460nm) in regeneration mode.

The advantage of fabricating an optical sensor is the possibility to decrease time regeneration. Sensor regeneration can be performed by exposing POF sensors to heat or/and blue light. In the present investigation, it has been found that for NO_2 gas sensing, polymetylosiloksane-graft-poly-3-(heksyltiophene) –graft-polyether sensor material has the optimum regeneration for using a light source with a wavelength of 460nm. Analyzing the effect of a short wavelength of a light source on POF heads coated with grafted polymers is the topic of our actual work.

In summary, a novel grafted polymer-coated thermoformed POF sensor head is proposed and demonstrated for the detection of NO_2 gas concentrations. We find that this structure is very sensitive to local chemical gas concentration, and the obtained sensitivities are below 1ppm of NO_2 in a dry atmosphere and low temperature. Such a small POF sensor could find applications in chemical sensing, such as trace analysis. The simple, dual step fabrication grafted polymer based optical sensor offers great manufacturing capability for monitoring low concentrations of nitrogen dioxide in different environments.

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References

[1] E. Maciak, Z. Opilski, M. Urbanczyk, J. de Physique IV **129**, 137 (2005).

[2] T. Pustelny, M. Procek, E. Maciak, A. Stolarczyk, S. Drewniak, M. Urbanczyk, M. Setkiewicz, K. Gut, Z. Opilski, Bull. Polish Acad. Sciences: Techn. Sciences, **60**(4), 853 (2012).

[3] G. Mauthner, K. Landfester, A. Köck, H. Brückl, M. Kast, C. Stepper, E. J. W. List, Org. Electron. Physics, Mater. Appl. **9**, 164 (2008).

[4] A.Stolarczyk *et al.* Polish patent application nr P.407784 RR10.

