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Optical interferometric structures for application in gas sensors

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In the paper, a gas optoelectronic sensor based on interferometric structure has been presented. Active polymer Nafion® layer deposited at the top of the optical fibre forms the Fabry–Perot interferometer. Interaction with gas changes the physical properties of sensing layer, hence the interference conditions are fulfilled for different wavelengths. Sensor performance for different humidity levels has been measured. The influence of humidity variations on sensing layer is investigated as well. In order to suppress the moisture induced instability of the sensor different inhibiting layers have been deposited and their performance has been investigated. In the paper, a wide investigation of the sensor in ammonia atmosphere has been shown.

Keywords: optical fibre sensors, optoelectronic gas sensors, optical interferometric structures.

1. Introduction

Optical methods in sensor systems have become popular since optical fibres, waveguides and other optoelectronic components became commercially available. Their distinct advantages, including electromagnetic noise resistance, high sensitivity, fibre optics compatibility, have proved their efficiency in many fields, to mention the most widely studied: temperature, strain and pressure sensors [1, 2]. Also, the gas sensor applications make the optical methods very challenging for researchers. The sensing principles of optical sensors are similar to the widely studied and commonly used electrical gas sensors. Namely, the interaction between gas and sensing layers changes the physical properties of layers.

The difference is in the properties which are to be monitored. In electrical solutions, it is usually monitored the resistance or conductivity, the capacitance, the electric field itself. In optical case, it is usually monitored the refractive index (both the real and imaginary part) that determines many measurands and different methods including reflected or transmitted light intensity [3, 4], interference spectra [5], surface plasmon resonance conditions (angle) [6], evanescence wave intensity [7], differential interference [8–13].

Both electrical and optical gas sensors exhibit the same features and problems to overcome for the researchers. The sensitivity to the chemical agents seems to be the most important factor. Also the selectivity must not be omitted in considerations, because it determines the sensor effectiveness in real environment. Another important factor is the ease with which the sensor recovers, which allows it to work continuously not only as a disposable indicator. The regeneration of the sensing layer can be achieved by exposure to an agent of opposite influence on the layer. The simplest way is the thermal annealing widely used in electrical sensors, which usually operate at high temperatures up to a few hundred degree centigrade. Unfortunately, the method requires external heating or equipping the sensor structure with a heat source. But this solution makes the sensors no longer all-optical, and it loses its main advantages. However, in some cases the process of recovery is intrinsic after the agent exposure has been discontinued.

The last but not least problem that will be taken into account, as far as the gas sensors are concerned, is the influence of moisture. Most of the designs reported have shown their good sensing abilities in low humidity. In electrical designs the problem vanishes with a high operating temperature. But in the case of low temperature optical devices, especially with organic layers, the humidity fluctuations are sometimes crucial for sensor operation.

The presented ammonia sensor is the optical fibre Fabry–Perot interferometer structure. The sensing Nafion®-layer exhibits the sensitivity to ammonia gas. Unfortunately, it is not immune to the humidity influence. The main task of this research was to observe the interaction with ammonia both at low and high humidity levels, as well as to analyze the response upon moisture variations, and to suppress this unwanted effect. In order to attenuate the influence of humidity, a few inhibiting layers (poly(methyl methacrylate) – PMMA, polyethylene, poly(isobutylene) – PIB, chitosan, polyvinyl acetate) have been deposited on the sensing layer and their efficiency has been measured.

2. Experimental

2.1. Sensor structure and operation

The sensor structure is presented in Fig. 1. The sensing Nafion®-layer deposited at the head of the fibre forms the Fabry–Perot resonant cavity. The mirrors are the boundaries between the air–Nafion® and Nafion®–fibre, respectively. Two beams reflected from both mirrors (including multiple reflections) interfere and the image is observed by the spectrometer.

In the case of Fabry–Perot interferometer the maximum location satisfies the equation:

$$m\lambda = 2dn\cos\alpha \tag{1}$$

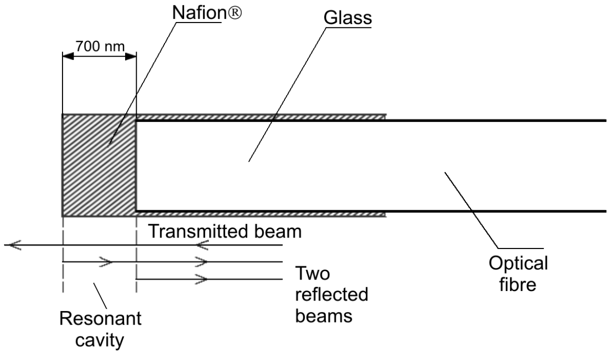

Fig. 1. The sensor head.

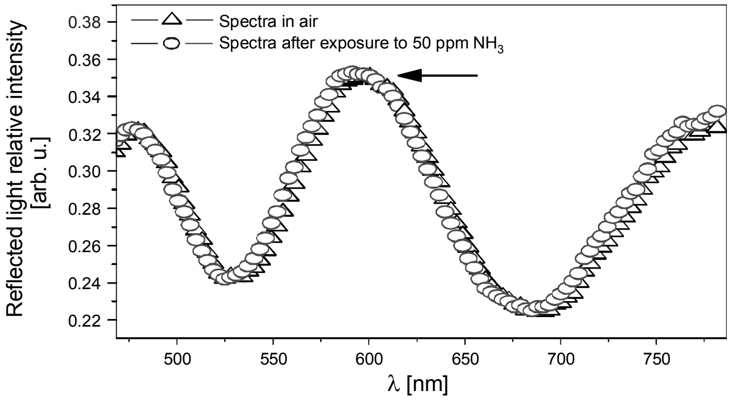

Fig. 2. The example of maximum location upon NH_3 exposure.

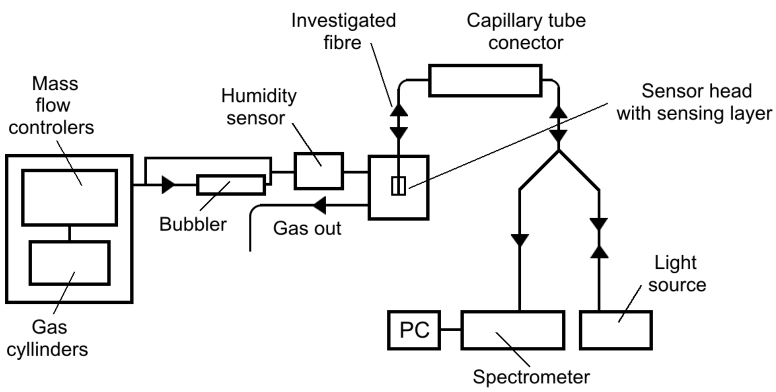

Fig. 3. The measuring setup.

where d and n denote the cavity thickness and the refractive index of material, respectively. The angle of incidence α relative to the fibre axis can be taken as 0°, making the $\cos\alpha$ equal unity, m stands for interference order ($m = 1, 2, 3, \ldots$).

The interaction with gas changes the optical properties and the thickens of the cavity. According to Eq. (1) the change in optical thickness affects the location of current maximum in wavelength domain. The variation of this location yields the sensor response to the changing environmental conditions. The exact analysis is performed by fitting the parabolic curve to measurement points and defining the vertex location.

2.2. Experimental setup

The measurements were performed in a setup presented in Fig. 3. The light source was an incandescent lamp. The gas flow system allows a stable moisture level to be provided by mixing dry (straight from the cylinder) and wet (passed through the bubbler) air in the appropriate ratio. The humidity sensor controls the moisture conditions.

3. Results

3.1. Response to ammonia at low humidity level

The results of measurement of the influence of ammonia on the sensing layer are presented in Figs. 4 and 5. The gas was a mixture of synthetic air and ammonia. The relative humidity level of air was about 4%.

The above results show that ammonia affects the Nafion® layer. The effect is almost fully recoverable after discontinuing the NH_3 exposure. The response is not a linear function of NH_3 concentration but it is unique and repeatable. The change in maximum location of about 3 nm, as show in Fig. 5, corresponds to the change of layer thickness

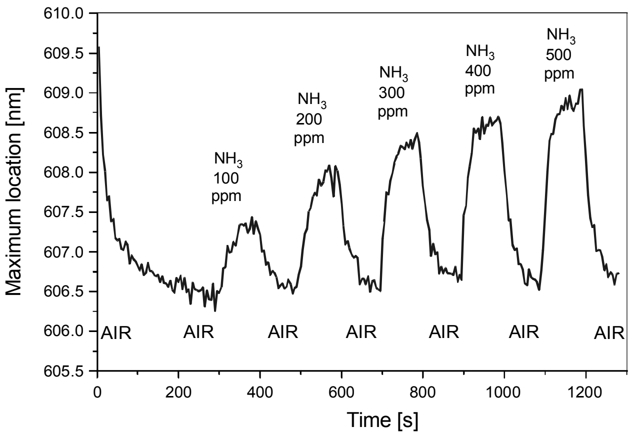

Fig. 4. Response to various NH_3 concentrations at low humidity level.

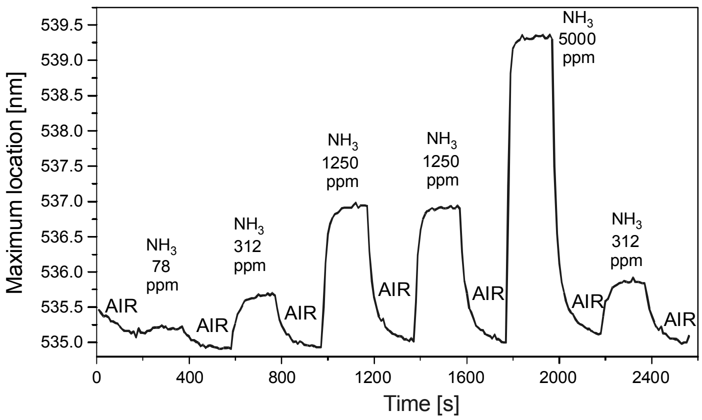

Fig. 5. Response to various NH_3 concentrations at low humidity level.

of 4 nm, or the change of refractive index of 0.003. It has not been determined yet which process takes place. The character of interaction is not clearly understood. The probable change in thickness is due to water absorption from NH_4OH, the presence of which is natural in the case of ammonia [9].

3.2. Response to ammonia at higher humidity

The interaction between ammonia and sensing layer at higher humidity is quite different. Figures 6 and 7 show that the optical thickness of the layer decreases with increasing NH_3 flow. According to the chemical reaction:

$$R–SO_3H + NH_4OH \leftrightarrow SO_3NH_4 + H_2O \tag{2}$$

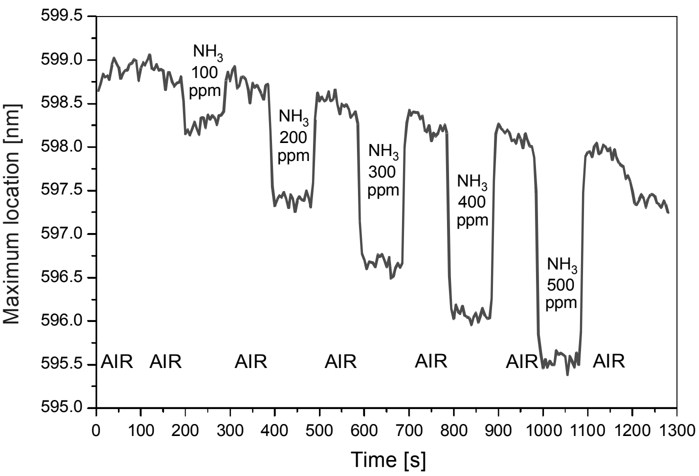

Fig. 6. Response to various NH_3 concentrations at 35% humidity level.

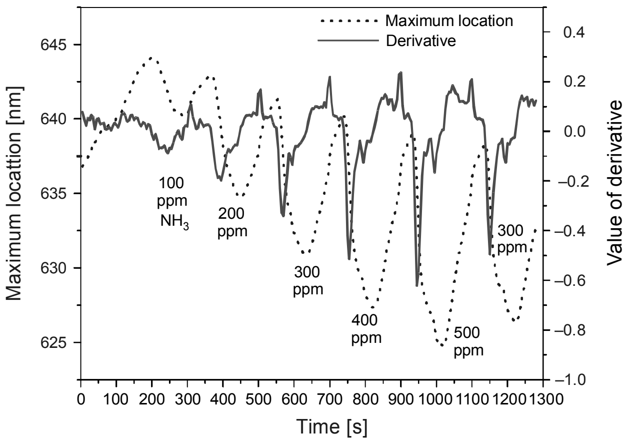

Fig. 7. Response to various NH_3 concentrations at 75% humidity level.

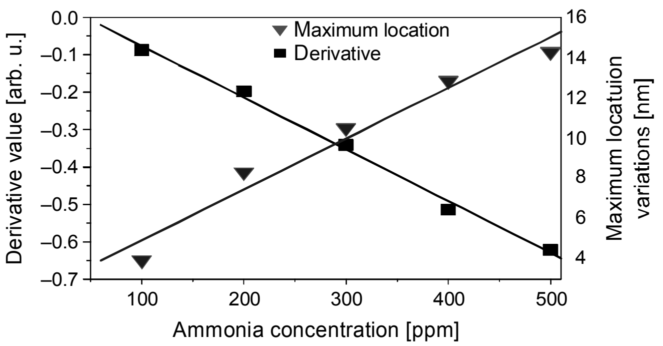

Fig. 8. Linear dependence of maximum location changes and its derivative versus ammonia concentration.

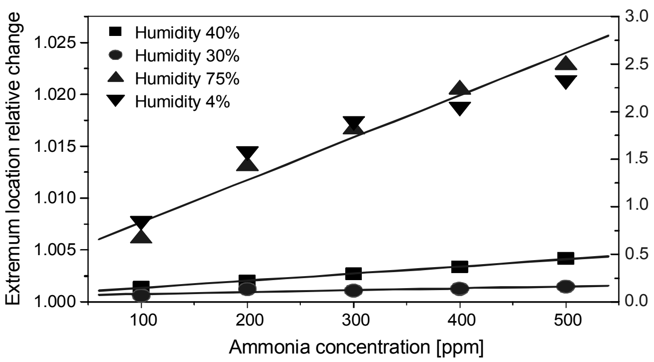

Fig. 9. Various linear dependences of relative maximum location changes for different humidity levels.

the thickness should increase as the salt SO_3NH_4 expands the polymer. The opposite change suggests that the refractive index changes. The problem will be investigated in further research.

The drift seems to be caused by saturation with ammonia. The response can be improved by differentiating the function of location versus time. The relative response is a linear function of NH_3 concentration, Fig. 8. The sensitivity for a current sample depends on humidity level, Fig. 9.

The second feature measured was ammonia permeability. Polyethylene is not transparent for NH_3 as well. Poly(methyl methacrylate) and poly(isobutyl) seem not to change the properties of Nafion® based structure. Chitosan reacts with ammonia in a similar way as Nafion®, hence it is meaningless using it as an inhibiting layer. The above results show that the layers measured are not suitable for moisture blocking.

4. Conclusions

The undesirable influence of humidity variations on a polymer sensing layer is crucial in the proposed low temperature optical sensor. Ammonia molecules bond water molecules and it is difficult to divide the effect of NH_3 and water reaction on organic layer. Under high humidity conditions the layer is saturated with water, and additional moisture from NH_4OH does not expand the layer as shown in Figs. 6 and 7. A better solution to moisture induced disturbances than blocking layer, might be to provide a stable humidity level. As shown on Figs. 8 and 9, the response to ammonia is a linear function of gas concentration. The sensor is a self-recovering structure. The stable moisture level would ensure good sensor performance. Better sensitivity to lower NH_3 concentrations can be achieved by differentiating the maximum location function or by other analysis methods such as neural network.

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