EFFECT OF HUMIDITY ON NH_3 GAS SENSITIVITY OF NAFION® /WO_3 SENSING STRUCTURE OF SPR SENSOR

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The paper presents an optical sensor that permits to detect and to measure the concentration of ammonia gas in a gaseous medium and the effect of humidity on the NH_3 detection capability of sensing structure of optical sensor was also investigated. The presence of water vapour, functioning as the interference gas, led to the lowering of the NH_3 response of the sensor in a humid atmosphere. An optical sensor of ammonia gas, based on the surface plasmon resonance (SPR) method has been investigated. The surface plasmon resonance (SPR) is very sensitive, and so is the optical technique used in chemical sensing. Nafion®/WO_3 stack films on plasmon active Au film was used as the sensing structure of SPR sensor. The gold layer was coated by means of vacuum evaporation on a BK7 substrate. The thickness of Au was about 50 nm. The sensing structures were coupled on immersion oil with a prism coupler. Although Nafion® film had hydrophilic character absorbs 22% by weight of water, the influence of humidity on the SPR sensor response was not as large as expected due to construction of the sensing structure. A change of the intensity of light of the plasmon dip was observed when chemical active stack films (Nafion®/WO_3) was exposed to varying concentrations of NH_3 in a dry and humid atmosphere. Optical ammonia gas SPR sensor display a very fast response time and a fast regeneration time at room temperature not only in a dry atmosphere, but also in a humid atmosphere.

*Keywords**:** SPR optical sensor, optical ammonia gas sensor, Nafion® film, tungsten trioxide thin film, humidity*

1. INTRODUCTION

The detection, measurements and control systems for pollutant and toxic gas emissions are nowadays very important for an ecologically responsible development. Another aspect is the control of the technological process, where dangerous substances are used as technological gases. Ammonia (NH_3) is one of the most important substances encountered in our daily lives. The major industrial application is in agriculture, specifically in the production of fertilizers [1, 2]. In the food industry ammonia is also an important indicator [2]. Recently, ammonia gas sensors based on different chemical interfaces and pH dye indicators have been developed. These chemical interfaces include metal oxide [1-9] and polymer films (especially conducting such polymers as PANi or PPy) [10-12] and pH indicators consisting of bromothymol blue or bromocresol purple [13, 14].

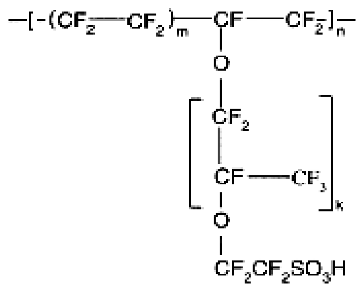

Fig.1. Structure of the Nafion®[11,20]

Transition metal oxides attract a considerable interest due to their suitability for use in a number of different applications, including gas sensors. These compounds exhibit a wide variety of properties, especially in the form of thin films. Metal oxides in the thin-film form are generally applied as gas sensitive materials [1–3] due to their reproducibility and typical surface properties suitable for gas detection.

Thin tungsten trioxide (WO_3) films deposited by means of various techniques (e.g. by sputtering, thermal evaporation or the sol-gel technique), are excellently applicable, especially as sensitive NO_x, NH_3, or H_2 gas layers [4, 5]. This is due to the fact that W transition metal has been found to occur in different states of oxidation (W^{5+}, W^{6+}) [4, 15-17].

Nafion® was developed by modifying Teflon® and was the first [20] synthetic polymer with ionic properties. Nafion® is very interesting ion exchange films. It is transparent for the UV-VIS-NIR region of light spectra. Fig. 1 shows the structure of the Nafion® film. It contains a fluorocarbon chain as the backbone of the membrane, which provides exceptional chemical, thermal and mechanical stability, while sulfonic acid groups ($-SO_3H$) with very strong ionic properties provide an ion exchange. Various types of sensors based on the Nafion® film has been described in literature [12,21-23]. Nafion® films respond mainly to humidity [21] and ammonia [22], resulting in products with dissimilar spectral characteristics. Thus, humidity surrounding a sensor utilizing Nafion® sensor film will influence the NH_3 detection capability of Nafion® films. Consequently, humidity is a parameter that must be dealt within the process of developing a reliable NH_3 sensor device.

In the present paper, we report the preparation and characterisation of an improved ammonia sensor with a better sensitivity and selectivity, using an amorphous ultra-thin WO_3 film covered Nafion® film. Using a very sensitive optical sensing technique, such as surface plasmon resonance (SPR) and a special configuration of the sensing structure were obtained interested results showing the influence of humidity on the SPR sensor response.

2. CONCEPT OF NAFION®/WO_3 SENSING STRUCTURE AND SPR NH_3 SENSOR

The idea of a layered sensing structure applied in optical sensors, as proposed by the authors, comprises the application of a ultra-thin film 6 nm WO_3 and a layer of Nafion®. The thickness of Nafion® layer was about 150 nm (Fig. 2). In the suggested structure of the sensor the successive layers have the following functions.

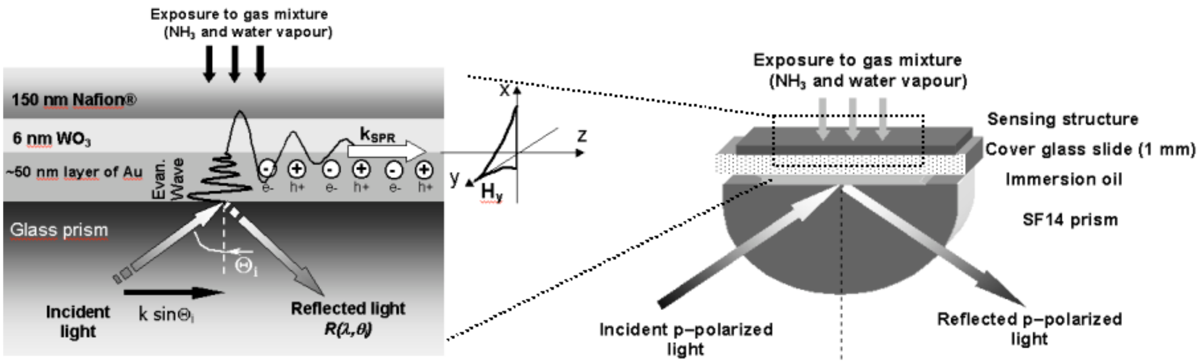

Fig. 2 Configuration of SPR sensor for ammonia gas detection.

Thin film of WO_3 is main receptor of ammonia gas in our sensing structure. As can be seen from Fig. 2, the design of the sensor is based on the fundamental concept of plasmon sensors in the system proposed by Kretschmann and Raether [18]. In this system surface plasmons are excited at the boundary between the Au layer and the 6 nm WO_3 above it. Plasmon waves propagating along the boundary between the thin Au layer and the WO_3 are called surface plasmon polaritons (SPP's) [18, 24]. The electromagnetic field vectors of the plasmon wave reach their maximum values at the interface Au/WO_3 and decay evanescently into both media. The main part of field of SPP is concentrated in WO_3. WO_3 strongly react with ammonia in air, therefore, the thin WO_3 film changes and optical properties as a function of the NH_3 gas concentration. The reactions of such processes are shown below [8, 9]:

$$\begin{gathered} O_2 + ne^- \rightarrow \left| O_2^-,\ \ O^-,\ \ etc. \right| (ads) \\ 2NH_3 + 3O^-(ads) \rightarrow N_2 + 3H_2O + 3e^-, \end{gathered} \tag{1}$$

where ne^- are free electrons in the WO_3.

Nafion® also strongly react with ammonia and water Gas that associates strongly with sulfuric acid will permeate through Nafion® based on this chemical affinity. Gases that are basic in character (as opposed to acidic ones) associate strongly with sulfuric acid (acids react strongly with bases). Fortunately for us, most bases are solids at the temperatures of interest for us. Bases usually have a hydroxyl group (-OH) as part of their molecular composition. Water (H-OH), organic bases called alcohols (general formula R-OH), and ammonia (when water is present) forms ammonium hydroxide by the reaction [20]:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-, \tag{2}$$

are the main gases that are basic in character and consequently permeate through Nafion®. Nafion® has different very important properties it is highly resistant to a large majority of chemical substances, like Teflon®.

SPR excitation by the incident of a light wave at the base of the prism occurs when the wave vector of the plasmon k_{SPR} and the length of projection of the wave vector of the incident wave in the direction of propagation of the plasmon are equalized, Eq. (3). The angle at which the surface plasmons are excited, and thus the angle, at which the attenuation of the incident wave is strongest, can be determined by means of the following formula [18, 19, 24]:

$$\begin{gathered} k\sin(\Theta_i) = k_{SPR} \\ k_0 \cdot n_{Prism} \cdot \sin(\Theta_i) = k_0\sqrt{\frac{\varepsilon_{Au} n_s^2}{\varepsilon_{Au} + n_s^2}}, \end{gathered} \tag{3}$$

where k_0 - length of the wave vector of light in a vacuum; k_{SPR} - length of the wave vector of the surface plasmon; n_s - refraction index of the dielectric medium above the metal layer; ε_{Au} – real part of the dielectric complex constant of the active plasmon layer (Au); n_{prism} - refraction index of the prism; Θ_i – incident angle of light on the prism base.

When $k\sin\Theta_i = k_{SPR}$, the momentum matching this condition and surface plasmons are created at the interface of the thin film gold/sensing stack. The formation of SPPs is mostly easily observed as the minimum in a plot of the reflectivity versus the incident angle and wavelength of illumination, Fig. 2. The formation of thin sensor films (WO_3 and Nafion®) on the Au surface shifts the SPP dispersion curve to larger k_{SPR} values, which in turn requires higher incident angles to satisfy the resonance condition of $k\sin\Theta_i = k_{SPR}$. This indicates that the length of the real part of the wave vector of the surface plasmons k_{SPR} depends on the refractive index of the metal layer and the refraction indices of the sensor films and their thickness above the metal layer. Moreover, k_{SPR} also depends on the gaseous dielectric medium above the thin sensor film. The presented optical SPR ammonia sensor is based on variations of the reflected spectral and angular plasmon minimim, resulting from the interaction of ammonia and water vapour with the Nafion®/WO_3 sensing stack on Au film.

3. EXPERIMENTAL RESULTS

Gold layers were coated by vacuum evaporation at 8^x10^{-6} Tr on a substrate 1 mm thick, made of a BK7 (*Schott*) glass slide. The thickness of Au was about 50 nm. Active thin films of amorphous tungsten trioxide (WO_3) were prepared by thermal evaporation of WO_3 powders of 99.99% purity (*Fluka*) from a molybdenum boat onto a 50 nm Au layer (Fig.2, 3.). The evaporation chamber was pumped to a vacuum of 1^x10^{-5} Tr. The sublimation, evaporation temperature was 700°C to 1000°C for WO_3 powder. The average rate of the film growth, controlled by a quartz monitor, was 1-2 nm/s. Film thickness of WO_3 amounted to about 6 nm. Fig. 6 presents the configuration of a SPR sensing structure based on an a-WO_3 sensor film.

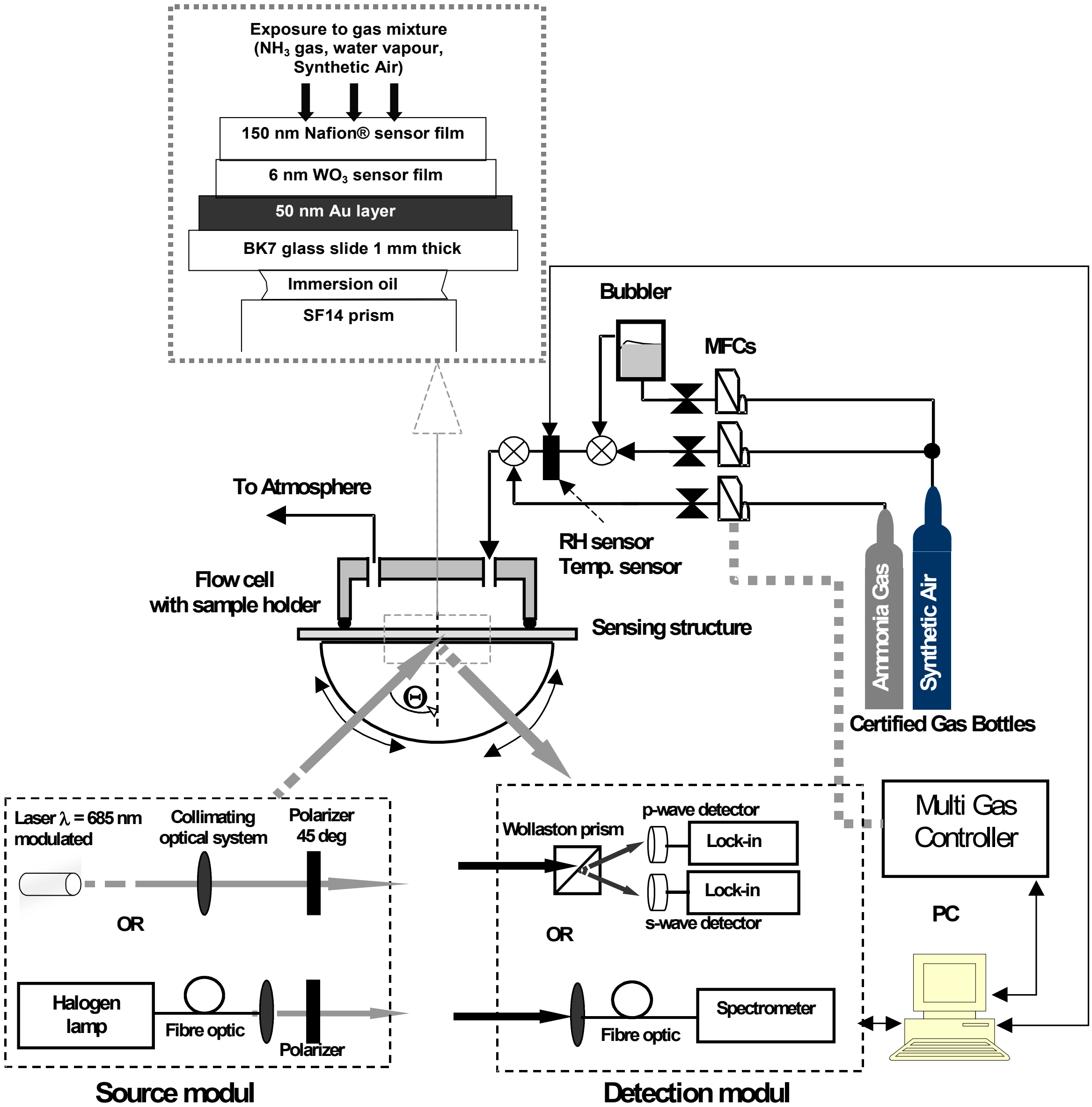

Fig. 3. The experimental set-up for measurements of variations in the optical signal of a light reflected from the sensor structures.

The Nafion® SPR sensor film was prepared by means of the spin-coating method. This method consists in the dissolution of the polymer in an adequate solvent; the solution is then spread on the rotating substrate. After evaporation of the solvent, there remains a thin layer of polymer, whose thickness depends on the solution viscosity, rotation rate and duration. 5% Nafion® solution of the mixture of water and lower alifatic alcohole was dropped onto the rotating Au + WO_3 BK7 glass slide. Glass plate is 1 mm thick. After the position of Nafion® layer glass plate was drying at 40°C for 2h, successively, followed by curing at 100° C for 15 minutes. The substrates with generated sensor structures were coupled on immersion oil with a cylindrical prism, made of SF14 glass (Schott). This prism ensured a mechanical stability of the optical system and warranted an adequate range of light-wave vectors. The dispersion of the refractive index of the oil was more or less the same as that of cover glass. Fig. 3 illustrates the configuration of the multi-layer sensing structure applied in our investigations of interference phenomena.

The measurement system employed in these investigations has been presented in Fig. 2. The idea of these measurements was to obtain reflection characteristics both as a function of the angle and the wavelength, as well as when exposed to a mixture of synthetic air (80 *%* N_2, 20 *%* 0_2) and ammonia and water vapour with a varying volumetric content. Gases with a purity of 99.99% were mixed in a stacker provided with *Bronkhorst H-Tech* mass flow-controllers. A gas server permitted the batching of the gas mixture with a precision exceeding 0.1 %. The gas mixture passed a (teflon) measuring cell with a volume of about 0.8 cm^3 at a speed of 1000ml/min. The tested sensor structures were placed on a goniometer permitting their angular scanning with an accuracy of the angle-setting exceeding 0.01 deg. The system also warranted an automatized determination of the incidence normal of the optical beam.

All these measurements were carried out at a room temperature of 20°C.

4. RESULTS AND DISCUSSION

The optical SPR characteristics were obtained by measuring the reflected optical signal of p-polarized light as a function of the incident angle and wavelength of light. Fig. 4 shows the results of dynamic measurements of the optical signal of the 150nm Nafion®/6nmWO3 stack in dry air. The gas mixture containing NH_3 gas dissolved in synthetic air with a cyclic change of concentrations from 0 ppm to 1000 ppm. These measurements were carried out for light with a wavelength of 685 nm, incident on the structure at an angle of 49.2 deg. At exposition to ammonia gas the optical response signal is fully reversible, Fig. 4. The obtained results have proved that such a sensor structure is sensitive even to ammonia concentrations below 25 ppm in dry air (<RH 2%). In dry air it operates almost without any delay. The

optical response of the sensor in a wide range of NH_3 gas concentrations is distinctly non-linear.

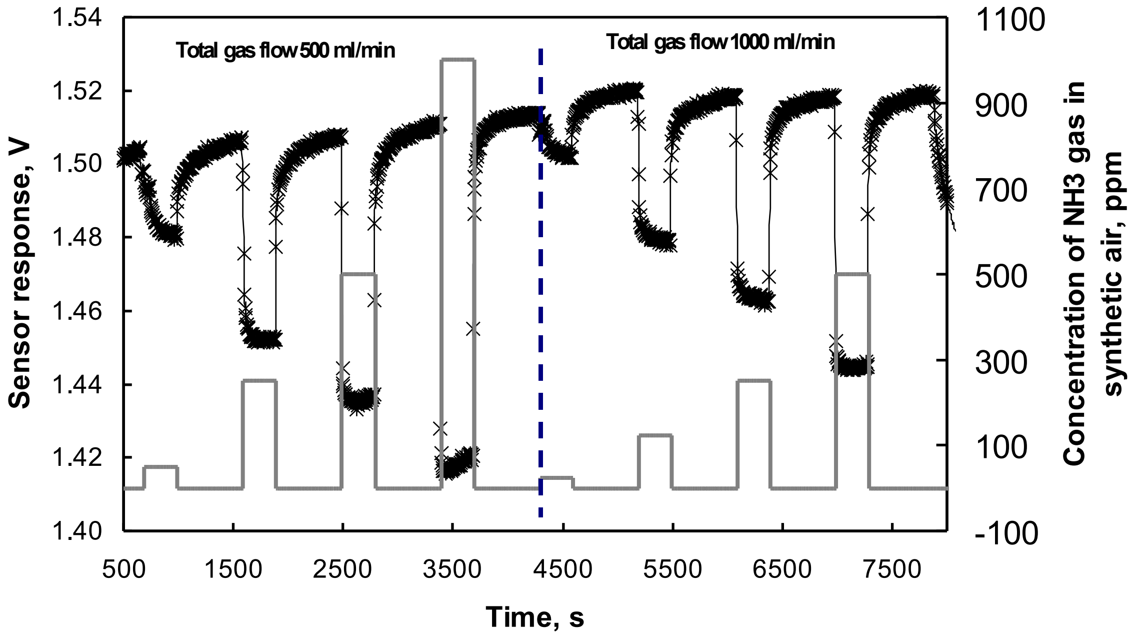

Fig. 4. The optical signal variation of the SPR sensor versus the time exposition varying concentrations of NH_3 at room temperature and dry air. Experimental conditions: p–polarized monochromatic light $\lambda = 685$ nm, incident angle of light $\Theta = 49.2$ deg.

a) b)

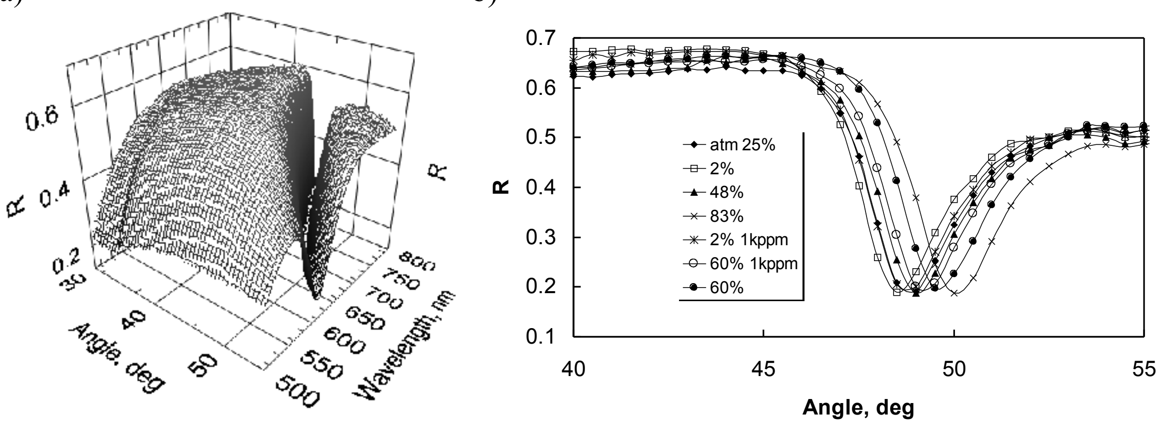

Fig. 5. Measured reflectance of sensing structure (a) as a function wavelength and angle of incident light for p-polarized light (air atmosphere RH 23%) and (b) for different concentrations of the water vapour and 1000 ppm of NH_3 in dry and wet (RH 60%) air, 685 nm p-polarized light.

Fig. 5a shows typical spectral reflectance of the investigated structure Nafion®/WO_3 as a function of the angle of incidence on the structure for surrounding atmosphere (RH 25%). Fig. 5b presents the reflection coefficient of the sample as a function of incident angle at 1000 ppm ammonia gas and at several relative humidities. The measurements were made after the sample being kept for 20 min in ammonia ambient or at selected relative humidities. It can be seen that, at different relative humidities, the sample's SPR resonant angle increases with the increasing humidity for λ = 685 nm. The SPR resonant angle also increases for the same wavelength and relative humidity with the appearing ammonia (1000 ppm).

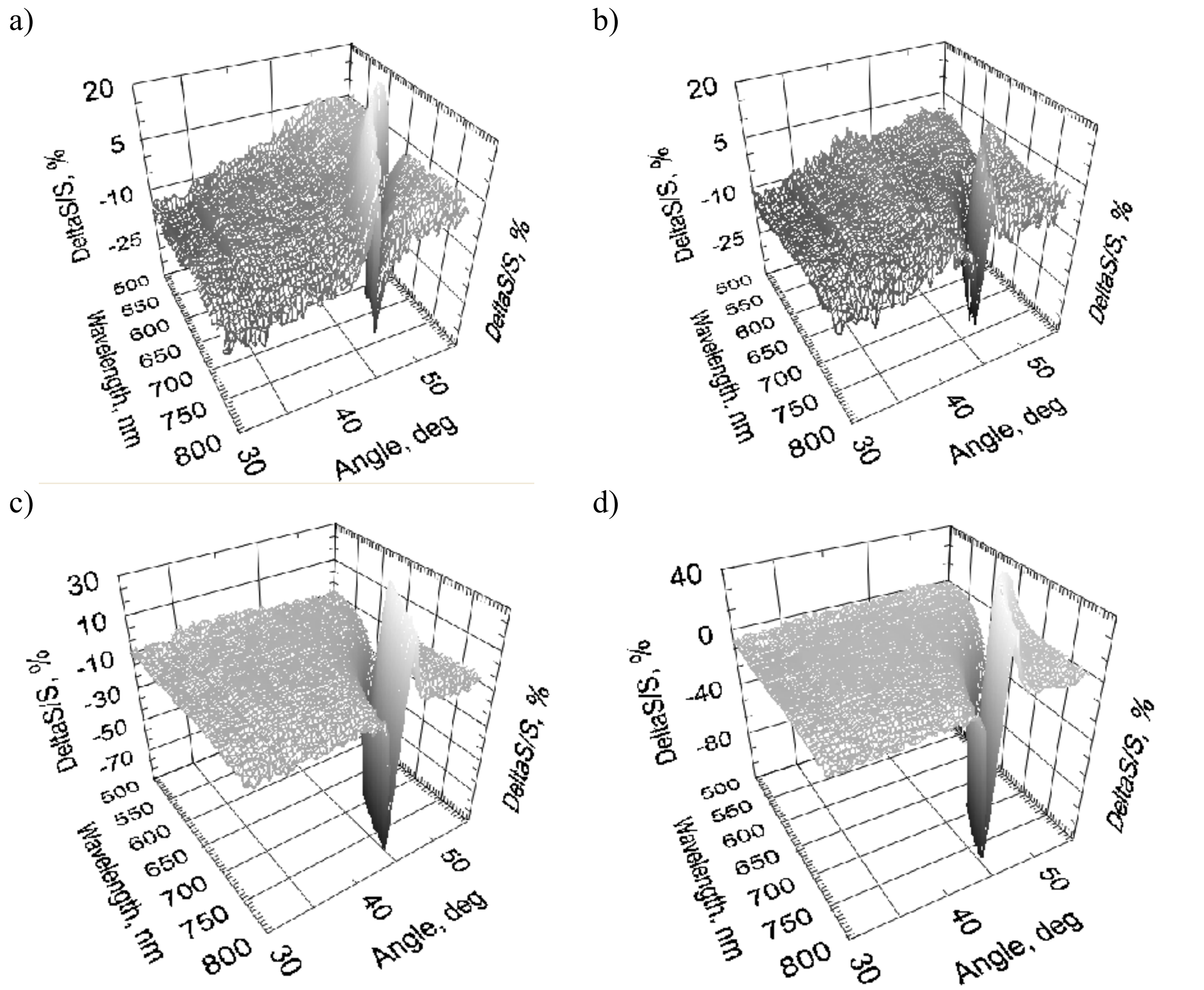

Fig. 6. Reflected light intensity change (in %) for the sensing structure as a function wavelength and angle of incident light for (a) RH 2% (dry air) (b) RH 48% (c) RH 60% (d) RH 83%. Structure was exposed to gas mixture flowing with 500 ml/min rate and consisting water vapour.

Fig. 6 presents a relative change of the optical signal *ΔS/S* the interaction in the investigated spectral and angular range due to the interaction of the structure and the synthetic air with different relative humidity from 2% to above 80%. The investigations concerned the visual range of spectra (500 nm - 780 nm). The relative change of the optical signal has been determined in compliance with the relation:

$$\frac{\Delta S}{S} = \frac{S_{ambient\_atm\_RH25\%} - S_{flow\_air\_RH\_X\%}}{S_{ambient\_atm\_RH25\%}} * 100(\%) \,. \qquad (6)$$

The structure was exposed to the dry and humid synthetic air for 20 minutes. After absorption of water vapour by Nafion® film the optical signal change within the range of the plasmon minimum because refractive index this layer has been changed. The variation of the signal is of essential importance, as was to be expected, in the range of plasmon minimum.

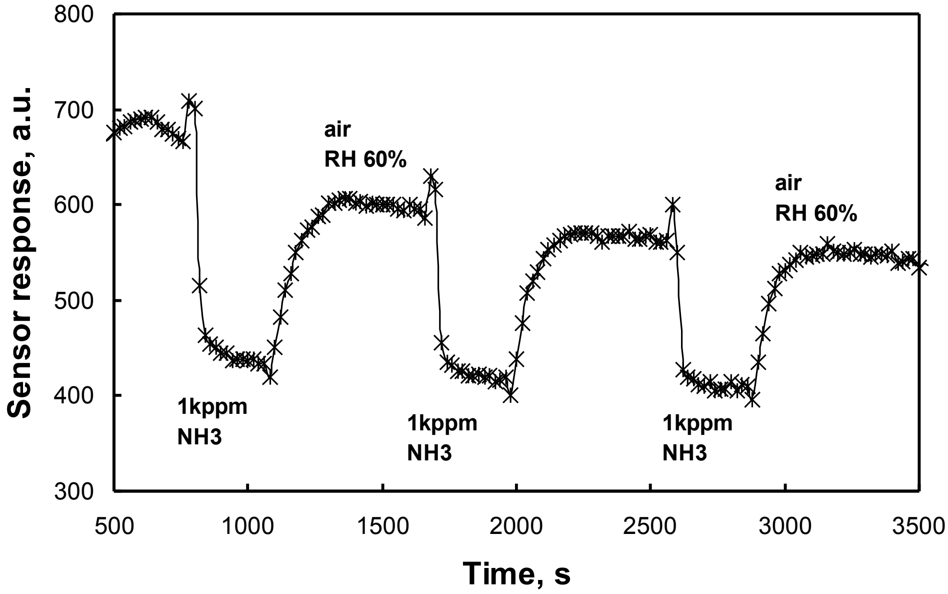

Fig. 7. The optical signal variation of the SPR sensor versus the time exposition varying concentrations of NH_3 at room temperature and humid air (60% RH). Experimental conditions: p–polarized monochromatic light λ = 685 nm, incident angle of light Θ = 49.2 deg.

The SPR sensor response of the sensing structure was measured at 1000 ppm of NH_3 in a humid atmosphere. A typical result measured in 60% RH obtained for Nafion®/WO_3 stack is shown in Fig. 7. After steady optical signal was obtained in air at 60% RH, the same humidity-controlled NH_3 was introduced in the measuring cell. The response curve appeared to be very similar to that observed in a dry atmosphere (see Fig. 4). These experimental results support the conclusion about the reaction of ammonia molecules on Nafion® in humid atmosphere. Generally, for "red" light sensor response of our SPR sensor increases with the increasing relative humidity; and at a given concentration of water vapour, the sensor's response decreases, as the ammonia concentration rises.

5. CONCLUSIONS

A new and original idea of the authors is the specific configuration of the layered sensing structure, sensitive to ammonia, which can be applied, in gaseous dry or humid environment.

In this paper, SPR Nafion®/WO_3 based sensor has been investigated at dry and humid air. The intensity of light change of a plasmon minimum was observed and quantified by the sensor when chemical active stack films change optical parameters by exposure to varying concentrations of NH_3 gas diluted in the dry and humid synthetic air. At room temperature

SPR optical ammonia gas sensor has generally a response time of less than 1 minute and a short regeneration time of less than 3 minutes. The excitation of SPR phenomena and monitoring of variations in the intensity of the plasmon dip arising due to the effect of ammonia gas make it possible to achieve a higher sensitivity of the structures than in the case of simple reflection sensors. The optical SPR sensors are sensitive to NH_3 gas below 30 ppm in synthetic air.

Although Nafion® film had hydrophilic character absorbs 22% by weight of water, the influence of humidity on the SPR sensor response was not as large as expected due to specific construction of the sensing structure.

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