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Sol-gel derived sensitive films for ammonia evanescent wave sensors

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The paper presents the results of investigation on the application of sol-gel technique to production of sensitive films. The sensitive films are made using silica SiO_2 in which an indicator is bound. Bromocresol purple was applied as the indicator. The films produced are sensitive to ammonia.

Keywords: ammonia sensor, evanescent wave spectroscopy, sol-gel.

1. Introduction

We have recently been witnessing a very intense development of optical planar waveguide chemical and biochemical sensors. Their structures are produced as multi-layer systems. On the planar or strip waveguide a sensitive film is deposited whose properties are changing with the concentration of a given chemical species. The light wave propagating in the waveguide is penetrating the sensitive film with its evanescent field. The change of the properties of sensitive film means therefore the change of propagation conditions of the light wave and hence the change of its parameters. This measurement technique is referred to as the evanescent wave spectroscopy [1].

Planar sensors can be realized in systems with phase detection or amplitude detection. There is a certain limitation involving the development of planar waveguide chemical sensors with phase detection, namely the lack of appropriate sensitive films for such sensors. Much more available are sensitive films for amplitude sensors. We can apply here, *e.g.*, metallophtalocyanines [2], polyaniline [3] or films produced with sol-gel technique, which are dealt with in the present paper.

The sol-gel technique provides great potential for the production of optical films of various refractive indexes, and it particularly involves two-component systems SiO_2:TiO_2 [4], [5]. Such films, depending on their optical and geometrical parameters, can be applied as waveguide films, masking films, and, when they change their properties under the influence of some external agent, they can be applied as sensitive films. The production of sensitive films for amplitude sensors is the easiest in a single -component system in which the silica SiO_2 plays the role of a matrix binding a respective indicator.

The problem involved in the design of such a sensor is limited either to the choice or development of an appropriate sensitive film and to optimization of the parameters of the sensor structure.

The paper presents the results of investigation on the technology of ammonia -sensitive films produced with the application of sol-gel technique. The sensitive films are obtained using the silica SiO_2, which is the matrix binding the bromocresol purple. The application of such films to ammonia sensors, but produced by means of a different technology can be found in [6]. In the present paper, we describe a technology of sensitive film production and the methods for measuring their properties. Our investigation concerns the influence of the rate of withdrawing substrate from solution on the thickness of the films produced and the influence of ammonia on the transmission characteristics of these films. We show the dependence of absorption coefficient of the film material and the expected dependence of mode attenuation of an exemplary sensor structure on the concentration of ammonia.

2. Sol-gel processing

2.1. Chemical basis

The sol-gel technique is a chemical method for the production of amorphous materials from solutions. The appropriate organic or inorganic compounds are precursors of these materials. For silica, the most commonly applied precursors are tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS) or tetramethoxysilane $Si(OCH_3)_4$ (TMOS). In our investigation, we applied TEOS (Aldrich, Germany) as the silica precursor.

The following stages can be distinguished in the film formation process using the sol-gel technique [4], [5]:

– formation of a colloidal system (sol) in which the precursor applied is a dissipated phase, with alcohol and water being appropriately used, for the latter;
– hydrolysis and gelation (polymerization);
– deposition of gel film on the substrate;
– drying and heating of the deposited films.

The processes of hydrolysis and gelation take place all the time, starting from the mixing of the input components until the heating of the films formed.

In the process of silica formation, the hydrolysis and polymerization are described by the following respective reactions:

$$Si(OR)_4 + H_2O \rightarrow HO\text{–}Si(OR)_3 + ROH, \tag{1}$$

$$(OR)_3Si\text{–}OR + HO\text{–}Si(OR)_3 \rightarrow (OR)_3Si\text{–}O\text{–}Si(OR)_3 + ROH \tag{2}$$

where R is an alkyl and OR is an alkoxy group.

The proportions of the input components applied, the kind and amount of the catalyst as well as the parameters characterizing particular stages of the technological process have influence on the properties of the films obtained.

2.2. Film formation by dip coating method

Three methods are used in the formation of films with the application of sol-gel technique: spin coating method, dip coating method and meniscus coating method [5]. In the present investigation, we used the dip coating method. The basic technological parameter in this method, which has an influence on the thickness of the film deposited on the substrate, is the rate v of substrate withdrawal from solution. Theoretical dependence of the film thickness d on the withdrawal rate, assuming that this rate is low, can be written in the following form [4], [7]:

$$d = Av^{2/3}, \tag{3}$$

in which

$$A = \frac{0.94\eta^{2/3}}{\sigma^{1/6}(\rho g)^{1/2}} \tag{4}$$

where: η – surface stress along the phase border gel solution–air, σ – viscosity of gel solution, ρ – concentration of the solution, g – gravitational acceleration.

When deriving the above relation, the evaporation of solvents has not been taken into consideration, and hence it is not always in good agreement with the experimental results. As presented below, good agreement between theoretical and experimental results is obtained by introducing an absolute term to relation (3)

$$d = Av^{2/3} + d_0. \tag{5}$$

2.3. Technology

The sensitive films described in the work were formed using silica, which makes up a matrix binding the indicator. In the investigation, bromocresol purple was applied as indicator. Tetraethoxysilane (TEOS) was applied as the precursor of the sensitive films produced, and the remaining input components were such as ethyl alcohol (EtOH) and water. Hydrochloric acid (HCl) was applied as catalyst. The molar proportions of input products TEOS: EtOH: H_2O: HCl were as follows: 1:4:8:0.04. The bromocresol purple ($C_{21}H_{16}O_5B_{12}S$) had been earlier dissolved in the ethyl alcohol applied in the ratio of 0.1 mole per 100 ml of alcohol.

The components were mixed and then the solution was left for 3 hours in the ultrasonic field at a temperature of 50 °C. Then the solution was cooled to room temperature. The films were deposited on glass substrates using the dip coating method. For that reason, a mechanical system was constructed which allowed the withdrawal of the substrates at a controllable rate. The withdrawal rate can be controlled within the range from $v = 0.1$ cm/min to $v = 20$ cm/min. As substrates, we applied a microscopic glass plate (Menzel–Glazer) of dimensions 76×25×1 mm^3. Substrate glass was subjected to cleaning procedures which consisted in: mechanical

cleaning in water with detergent added to it, rinsing in deionized water, soaking in acetic acid, rinsing in deionized water, soaking in water with ammonia, rinsing in deionized water, rinsing in acetone and drying. The gel solution from which the substrates were drawn out was in a beaker and the whole was placed in a glass cylinder. Due to the above procedures the influence of accidental air movement was avoided, and in consequence, the production of homo-geneous films could be ensured. Due to the decomposition temperature of bromocresol purple (180 °C), the films obtained were heated at a temperature of 150 °C. The heating time was 2 hours.

3. Measurement methods

Thickness. The measurements of the film thickness were carried out using the interference method. On the films produced, a fault of the thickness equal to the thickness of the film was made by scratching the films. Then, in the process of vacuum evaporation, a thin film of aluminum was deposited on them. The height of the fault, equal to the film thickness, was determined from the shift of interference lines. The measurements for each film were carried out in several different places, for two wavelengths $\lambda = 537$ nm and $\lambda = 588$ nm. The thickness of the film was obtained as the average of the measurements carried out.

Refractive index. The refractive index of the films was determined using Abeles's method [8]. This method consists in determination of Brewster's angle for the film material. For this purpose, a light beam of polarization p is used and dependence of the reflected beam amplitude on the incidence angle is recorded for the two cases: when the beam falls on the substrate and when the beam falls on the substrate with the deposited film. When the light beam falls on the film at Brewster's angle, then the whole power passes into the film. Hence the amplitude of the reflected beam is the same as the amplitude of the beam reflected from the substrate on which there is no film. Therefore, the angle corresponding to the crossing point of both recorded characteristics is equal to Brewster's angle.

Sensor characteristics. The testing of sensor properties of the films produced consisted in determining the dependence of the film absorption on the wavelength and then determining the dependence of the film absorption for a given wavelength on the concentration of ammonia. In both cases the tests were carried out in a transmission system. A diagram of the measuring set-up which was applied to test spectral properties of the films is presented in Fig. 1. The substrates with sensitive films deposited on both sides were placed in a measurement chamber. The light of the wavelength λ was passed from the monochromator to the measurement chamber through a multi-fiber waveguide cable. A tungsten lamp was used in the monochromator as light source. A silica photodiode BPYP 17 (ITE, Poland) was used as a detector. The measurement signal was measured with a voltmeter. In the tests on spectral properties, the maximum concentration of ammonia was used, which was effected by passing the air through the water solution of ammonia of 25% concentration which was in the bottle. The air was driven by a pump. In the tests concerning the dependence of absorption of the film

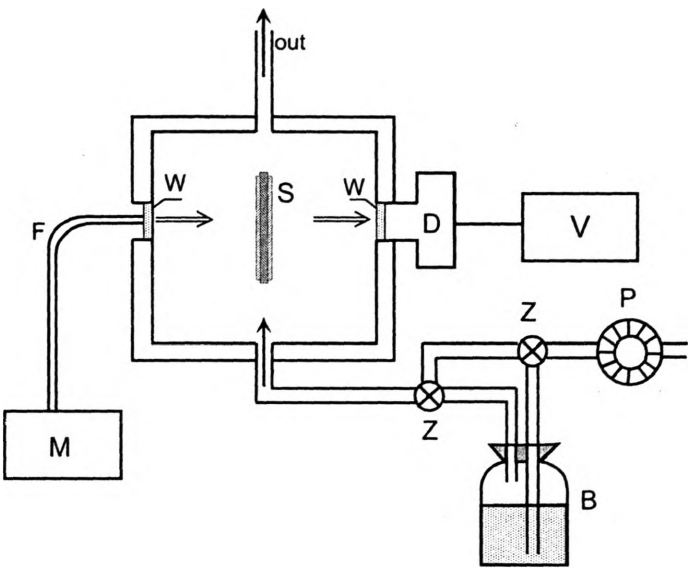

Fig. 1. Diagram of the measuring set-up for testing the transmission of sensitive films: M – monochromator, V – voltmeter, F – optical waveguide cable, D – detector, W – silica windows, S – structure with sensitive film, Z – valves, B – bottle with ammonia water, P – pump.

on the concentration of ammonia, instead of a monochromator, a LED was applied as well as a gas feeding system which allowed changing the concentration of ammonia from $\eta = 0$ ppm to $\eta = 5000$ ppm.

4. Results

The influence of the rate of substrate withdrawal from gel solution on the film thickness d is presented in Fig. 2. The crosses stand for experimental points. The solid line is used to mark their approximation with the function of the dependence character $d(v)$ defined by Eq. (5). The following was obtained from the matching using the least squares method:

$$A = (72.2 \pm 0.4)\ \text{nm}\left(\frac{\text{min}}{\text{cm}}\right)^{2/3}, \qquad d_0 = (39.1 \pm 0.1)\ \text{nm}. \tag{6}$$

It can be seen from the relations presented in Fig. 2 that in the applied range of rates v, Eq. (5) is in very good agreement with the experimental results.

The experimental results obtained show, in accordance with theoretical predictions, that together with an increase of the withdrawal rate of substrate from gel solution the thickness of the film produced increases. At the substrate withdrawal rate of $v = 1.56$ cm/min the film thickness was $d = 135$ nm, whereas at the withdrawal rate of $v = 4.25$ cm/min the thickness of the sensitive film was $d = 230$ nm. The refractive index of the films produced was determined as $n = 1.44 \pm 0.02$.

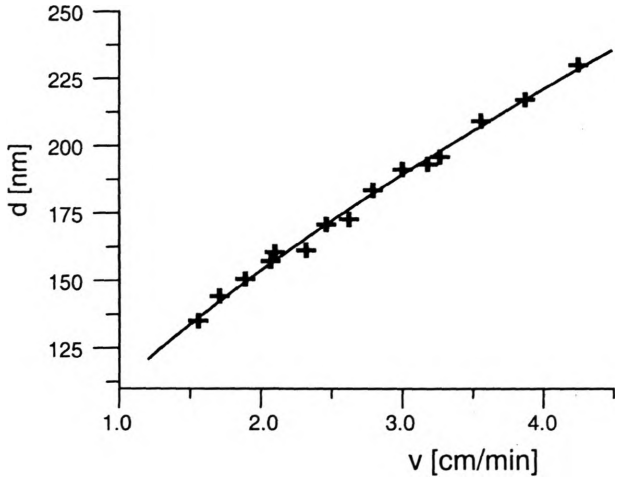

Fig. 2. Dependence of sensitive film thickness on the withdrawal rate of substrate from solution.

Spectral properties of the sensitive films produced were investigated in the measuring system presented in Fig. 1. The investigation was carried out at room temperature (20 °C). For each thickness of the sensitive film, two characteristics were determined involving the dependence of transmission on the length of light wave. The first characteristic was determined when the measuring chamber was filled up with air. The second characteristic was determined when the measuring chamber was filled up with air containing ammonia of the maximum concentration (the air was passed through ammonia water of 25% concentration).

The bromocresol purple (dye) subjected to the influence of ammonia in the presence of water vapour changes its colour from orange to purple. This process is described by the following chemical reactions [10]:

$$NH_3(\text{vapour}) + H_2O \leftrightarrow NH_4^+OH^-, \tag{7}$$

$$NH_4^+OH^- + H^+Dye^- \leftrightarrow NH_4^+Dye^- + H_2O, \tag{8}$$

$$NH_4^+Dye^- \leftrightarrow H^+Dye^- + NH_3(\text{vapour}). \tag{9}$$

Exemplary results of transmission tests of sensitive films are presented in Fig. 3. It gives two transmission characteristics (curves 1 and 2) and the absorbance diagram. The characteristic 1 shows the dependence of transmission on wavelength λ when the film is located in the air. The characteristic 2 presents the transmission of the film subjected to the influence of ammonia of the maximum concentration. It can be seen that in the atmosphere containing ammonia the transmission of the film decreases in wide spectral range. Such changes are observed from $\lambda = 500$ nm to $\lambda = 700$ nm. In the presented runs, the characteristic of photodetector was taken into consideration.

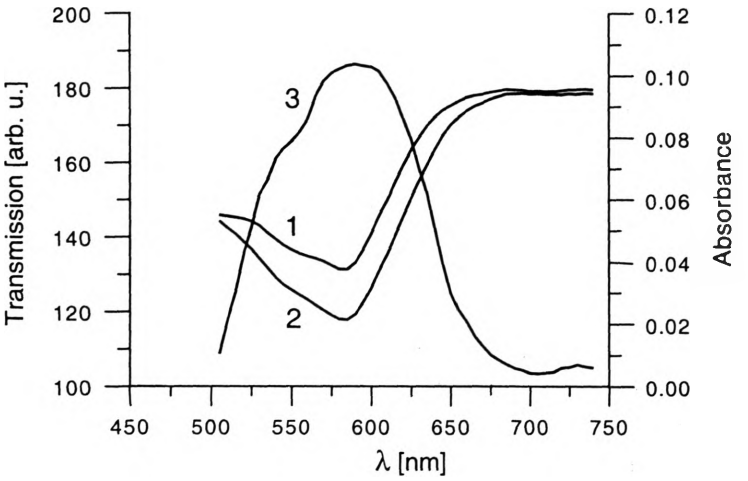

Fig. 3. Dependence of transmission and absorbance on wavelength for the sensitive film of the thickness d = 1280 nm. Curves: 1 – layer in the air, 2 – layer in the vapours of ammonia water, 3 – absorbance.

The characteristic 3 presents the dependence of absorbance on wavelength. It was calculated from the following relation:

$$\text{Absorbance} = \frac{I_{\text{air}} - I_{\text{amonia}}}{I_{\text{air}}} \tag{10}$$

where I_{air}, I_{amonia} are the transmissions for air and air with ammonia, respectively.

It can be seen that the absorption index α strongly depends on the wavelength, and for λ = 600 nm it has the maximum value. Therefore, the application of light source of the wavelength close to λ = 600 nm in the ammonia sensor is one of the requirements ensuring maximum sensitivity of the system.

Making use of the Lambert–Beer law

$$I_{\text{amonia}} = I_{\text{air}} \exp(-\alpha d) \tag{11}$$

and of the Eq. (10) we obtain the expression for absorption coefficient

$$\alpha = -\frac{1}{d} \ln(1 - \text{Absorbance}) \tag{12}$$

where d is the summary thickness of sensor layers.

When we know the absorbance of a given layer as well as its thickness, we can determine from Eq. (12) the dependence of absorption coefficient α on wavelength λ. The said dependences were determined for different summary thickness values of layers being investigated. The absorption coefficient α of the produced SiO_2 layers doped with bromocresol purple was accepted as the arithmetic average of absorption coefficients of the layers under investigation. Determined in such a way the dependence of absorption coefficient α on wavelength λ is presented in Fig. 4.

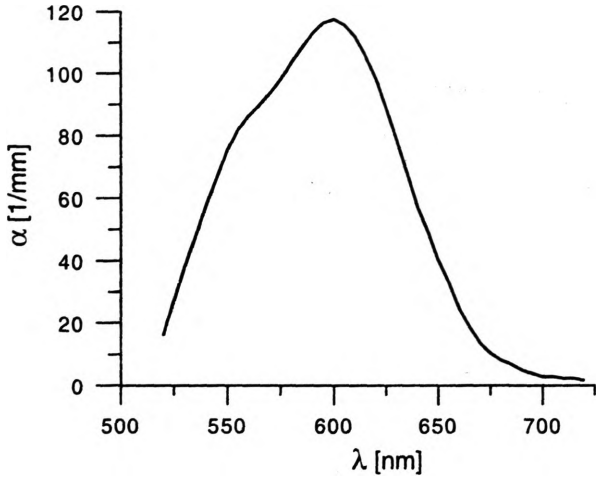

Fig. 4. Dependence of absorption coefficient α on wavelength λ for the sensitive film subjected to the influence of ammonia of the maximum concentration.

We must emphasize here the fact that the relation $\alpha(\lambda)$ presented in Fig. 4 determines an increase in absorption of the sensitive film material subjected to the influence of ammonia of the maximum concentration. Therefore, the increase of film absorption, in particular for the wavelength close to $\lambda = 600$ nm, is very big. The maximum value of the absorption coefficient equals $\alpha = (118 \pm 27)$ 1/mm. By calculating from the above the attenuation of the film material we can see that for the wavelength $\lambda = 600$ nm the attenuation of the film material subjected to the influence of ammonia of the maximum concentration increases by over 500 dB/mm.

The aim of the next series of investigation was to determine the influence of ammonia concentration on the absorption coefficient of the sensitive film for optimum wavelength and to check if the saturation of the response of sensitive film was not taking place when it was subjected to the influence of high concentrated ammonia.

When selecting the wavelength we allowed for diodes LED available on the market. The criteria taken into consideration when selecting an appropriate diode included, on the one hand, the wavelength (possibly close to $\lambda = 600$ nm) and, on the other hand, the parameters of the beam, which would in the future make it possible to apply this diode in the waveguide ammonia sensor. Having analyzed the available diodes, we selected the diode EL 383-2UYOC (ELFA), which emits light of the wavelength 611 nm, has light intensity of 11 cd and beam luminescence angle of 3 angular degrees. The investigation into the dependence of absorption coefficient on the concentration of ammonia was carried out by placing several substrates with the deposited films in the measurement chamber presented in Fig. 1. In this case, the LED diode ($\lambda = 611$ nm) had been selected as light source, and the ammonia of a given concentration was fed to the measurement chamber using the feeding system described in [10]. Nitrogen with water vapour added was applied as carrier gas.

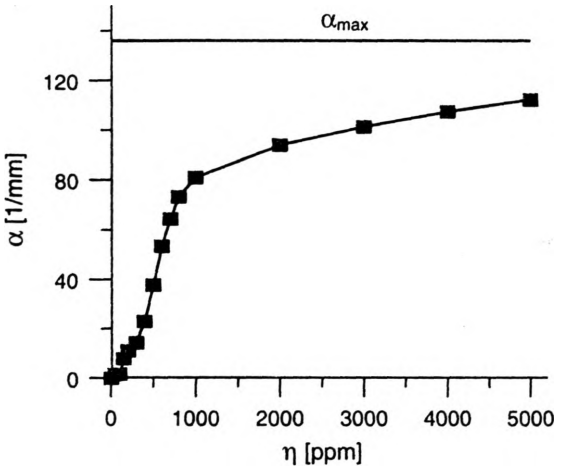

Fig. 5. Influence of ammonia concentration η on absorption coefficient α of sensitive film. Sensitive film (SiO_2 doped with bromocresol purple) produced in sol-gel technique on glass substrate. Film thickness $d = 3.3$ μm, wavelength $\lambda = 611$ nm.

The dependence of absorption coefficient α on the concentration of ammonia, determined on the basis of measurement data is presented in Fig. 5. The squares stand for measuring points. Two ranges corresponding with different dynamics of absorption coefficient changes can be seen on the characteristic. In the first range we can see a rapid increase of absorption coefficient together with an increase in ammonia concentration η. With an increase in ammonia concentration from $\eta = 0$ ppm to $\eta = 1000$ ppm, the absorption coefficient of the film increases from $\alpha = 0$ 1/mm to $\alpha = 81$ 1/mm. Further increase of ammonia concentration results in a considerably smaller increase of absorption coefficient. For the concentration $\eta = 5000$ ppm, the absorption coefficient of the film reaches the value $\alpha = 112$ 1/mm. A solid line was used to mark the level of absorption coefficient of the film material ($\alpha_{max} = 136$ 1/mm) determined for the case when the ammonia of maximum concentration was fed into the chamber. In the tests the results of which are presented in Fig. 5, we applied sensitive films, which were produced in a separate technological process, different from the ones presented above. Absorption coefficient α_{max} for this case within the measuring error is in accordance with the one which results from the characteristic presented in Fig. 4.

Figure 6 presents a theoretically calculated dependence of attenuation α_s of fundamental modes TE_0 and TM_0 in the sensor structure on ammonia concentration. In the calculations, we referred to the structure consisting of a planar waveguide with the sensitive film described above, of the thickness $d = 200$ nm. The waveguide referred to in the calculations was the planar one, which can be obtained in the ion exchange K^+–Na^+ in BK7 glass, in the process lasting 67 h at a temperature 400 °C, when potassium nitrate KNO_3 is used as admixture source. As can be seen from the

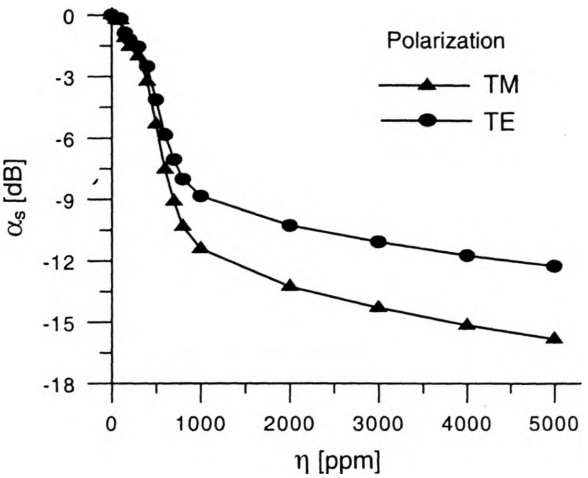

Fig. 6. Influence of ammonia concentration on the attenuation of fundamental modes in the sensor structure. Parameters of the structure: planar waveguide corresponding with ion exchange K^+–Na^+, process time 67 h, temperature 400 °C, sensitive film thickness d = 200 nm. The length of interaction path is 3 cm.

calculations, in the first measuring range, the attenuation of modes is extensively increasing with an increase in ammonia concentration, reaching for the concentration $\eta = 1000$ ppm the values $\alpha_s = -8.8$ dB for the mode TE_0 and $\alpha_s = -11.4$ dB for the mode TM_0. As presented in [11], by optimizing the parameters of sensitive film (thickness and refractive index) and the parameters of gradient waveguide, we can adjust within a very wide range the attenuation coefficients of modes in the sensor structure and hence the characteristics of the sensor. Such studies are in the realization phase and their results will be published in the near future.

5. Summary

The paper presents the results of investigation on ammonia-sensitive films. The films were produced using silica SiO_2, being the matrix binding the indicator, which was bromocresol purple.

In the paper the technology of these films has been described. The influence of the withdrawal rate of substrate from gel solution on the thickness of sensitive films obtained has been presented. The dependence of absorption coefficients α on wavelength λ is presented for the maximum concentration of ammonia as well as the dependence of absorption coefficient on ammonia concentration. It is demonstrated that the sensitive films presented can be applied within a very wide range of ammonia concentrations.

The sensitive films can be applied to planar sensors of ammonia. The knowledge of the dependence of absorption coefficient on wavelength $\alpha(\lambda)$ is indispensable in the designing phase of such sensors. At present, the author together with his team is

carrying out research works on the structure of amplitude sensor of ammonia which would be insensitive to excitation way.

The sensitive films presented in the work are in the development stage. Further research on the absorption sensitive films will be concentrated on the aging studies involving these films and on the application of other indicators. The aim of these studies will be to elaborate sensitive films resistant to unfavourable environmental factors in which they are expected to work.

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