SURFACE PLASMON RESONANCE PHENOMENA AND ITS APPLICATION FOR METALPHTHALOCYANINE SENSOR LAYERS INVESTIGATIONS

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The surface plasmon resonance spectroscopy is a technique that is capable of monitoring chemical and physical processes. It is sensitive to detect small changes of dielectric properties in a metal-phthalocyanine boundary. For this reason plasmon resonance phenomena have been used to characterize a number of different types of films. This work analyses the possibility of using the surface plasmon resonance phenomena in the detection of gas. Thin films of copper and lead phthalocyanines have been examined in the plasmon system from the point of view of their application in NO_2 sensors.

Keywords: surface plasmon resonance, dioxide nitrogen detection, phthalocyanine

1. INTRODUCTION

Industrial activities and the development of municipal agglomerations have resulted in the occurrence of quite a number of chemical substances in the air, among them such gaseous substances as nitrogen oxides, which are highly noxious compounds, endangering both man and the environment. The toxicity of these compounds and their abundance among other poisonous gases require new technical solutions concerning the structure of nitrogen-oxide sensors [1,2]. The technical development of systems monitoring the air aims at constructing such devices which might be widely used in industrial and environmental measurements. From among numerous new measuring techniques of toxic gases [2] in the group of optical methods the surface plasmon resonance spectroscopy deserves special attention. The fundamental element of this method is the plasmon sensor, consisting of metallic and semiconductor layers deposited on a dielectric substrate [3-6]. This idea, applied in the plasmon sensor, makes use of the changes of optical properties in the sensoring layer brought about by changes of the concentration of ambient gases. These changes are recorded by means of the plasmon resonance phenomenon (SPR) [3,4]. The phenomenon of plasmon resonance is connected with the occurrence of the surface plasmon wave which is the oscillation of the

electrical charge density in the metal layer. Such a wave may arise and keep at the interlayer of two substances metal-dielectric as well metal-semiconductor, when an electromagnetic wave strikes the surface. The idea of the operation of plasmon sensor consists in the equalization of the propagation constants of the plasmon wave (β_{SPW}) and the propagation constant of the electromagnetic optical wave ($\beta_{e\text{-}m}$) [6]. Therefore, the exciting electromagnetic wave is directed towards the interlayer of these two media through some material with a higher refracting index (e.g. glass, plastics) at the adequate angle $\theta(\lambda)$, characteristic for the given frequency (the light wavelength). Such a matching of the wave vectors warrants a resonance transfer of electromagnetic energy from the incident wave to the surface plasmon wave. Therefore, changes in the optical parameters of the investigated medium can be detected by analysing the intensity of the optical wave, which interacts with the surface plasmon wave (SPW).

Basing on our previous investigations and on references derived from literature [5-14], it results that molecular crystals, to which metallic phthalocyanines belong, display a high sensitivity to oxidizing and reductive gases, including NO_2. The sensitivity of the phthalocyanine layers depends on the morphological structure of their surface and on the type of the central atom in the macroring of the phthalocyanine [8].

The aim of the present paper was to investigate the reaction of phthalocyanine films deposited on a thin gold layer to the effect of nitrogen dioxide, in order to determine the sensitivity characteristic, making use of the plasmon resonance. Moreover, investigations have been taken up concerning the regeneration of the optical layered structures with phthalocyanine after their previous retention in an NO_2-atmosphere. Such investigations were carried out at NO_2-concentrations of 100 ppm in nitrogen for two different metellic phthalocyanines, viz. copper and lead phthalocyanines, with differing their films thicknesses and different conditions of their deposition.

2. EXPERIMENTAL INVESTIGATIONS

2.1. The idea of measurements and diagram of the measuring stand

In these investigations an optical measurement system was applied basing on Kretschmann's idea of such a system [15]. The tested sample in the form of a thin-layer NO_2-sensor (Fig.1) is placed on a goniometric table. On one side the sample is coupled with a prism, on the other with the chamber into which gases with a known composition are pumped in. The gases were batched by means of a coupled computer of programmer mixing the gases. At a flow rate of the gases through the chamber amounting to 1 l/min, the NO_2-concentration was controlled with an accuracy of about 0.5 ppm.

In the system mass flow controllers (MFC) were applied, controlled by a microprocessor. The measuring system is lighted by a source of white light. The light going by optical fiber , strikes which strikes on the prism where was reflected from the surface of the sensor and falls into detector. The signal from the detector was sent to the spectrometer and next recorded by the computer.

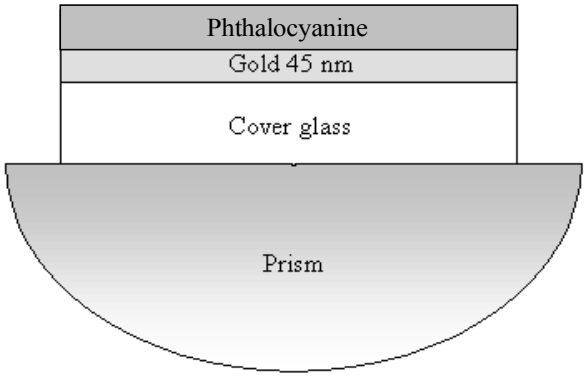

Fig.1 Lamellar structure with a sensor layer of phthalocyanine.

The idea of the test stand is to be seen in Fig.2. A detailed description of such a measuring stand and its diagram in [5,7] have been presented.

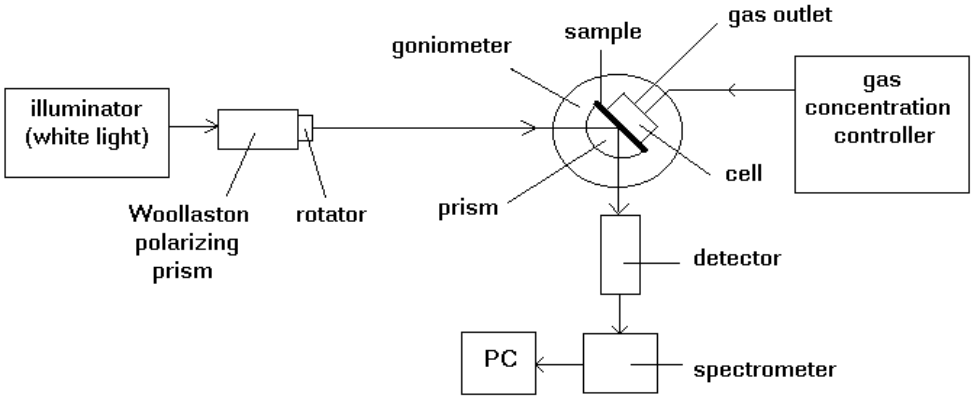

Fig. 2 Diagram of the measuring stand.

Thanks to the application of goniometer controlled by a computer, this measuring system permits to measure simultaneously the signal values on the detector as a function of the wavelength and the function of the angle between the sample and a light wave vector for all light spectrum during one, this same measurement series. The application of a spectrometer (WCad 3 type) permits to measure the signal from the detector over the whole spectrum of visible light. The numerical program, developed for the purpose of analysing the obtained

results make it possible to present the results in the form of three-dimensional diagrams of the sensitivity dependence of the tested structure for gas action on the light wavelength and on the position angle of the sample. Results of this kind concerning investigations of lead phthalocyanines in [7] were presented. The present paper deals with the sensitivity of sensor structures with copper and lead phthalocyanines to NO_2 actions.

The sensitivity of the structure to NO_2 is defined as:

$$S = \frac{\Delta R}{R_1} = \frac{R_2 - R_1}{R_1} \quad ,$$

where:

R_1 - intensity of the light signal from detector during the stay of the phthalocyanine sensor layer in nitrogen,

R_2 - intensity of the signal during the stay of this same sensor layer in a mixture of nitrogen and nitrogen dioxide for the tested concentration.

The theoretical analysis presented in [6] indicates that the characteristics of the resonance of plasmon structure as a function of the wavelength is a resonance one. In the case of the angle of incidence, at which the detector records a minimal signal, in the given sensor layer the most intensive resonance absorption of the electromagnetic energy of the wave striking the structure occurs in favour off the surface plasmon wave [3-6].

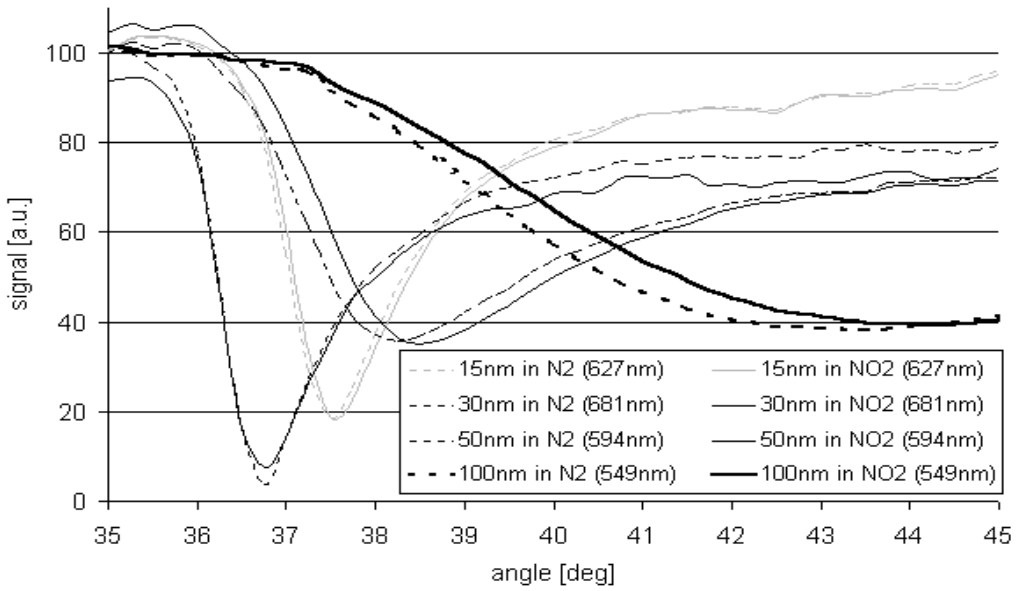

Fig. 3. Signal in the detector as a function of the detection angle with visible plasmon minima in the case of PbPc with thickness of: a) 15nm; b) 30nm; c) 50nm; d) 100nm, tested in N_2 and in the mixture N_2 and 100ppm NO_2.

According to investigations presented in [7] the angle at which resonance absorption of the electromagnetic wave occurs, changes its value with the change of phthalocyanine film thickness in the lamellar structure of the sensor. Fig.3. presents the obtained results concerning lead phthalocyanine.

2.2. Resonance of the sensor layer with copper phthalocyanine on a substrate of gold having been exposed to nitrogen dioxide

Sensor structures were used in the experiments, consisting of a layers of gold and copper phthalocyanine deposited on a glass substrate by means of vacuum evaporation. The temperature of the substrate was about 27°C (300K). The gold layer was 45nm thick, that of phthalocyanies 10 to 120nm. Phthalocyanine was deposited by vacuum evaporation in compliance with a previously settled rate characteristic of evaporation at 300°C [7].

Investigations carried out on copper phthalocyanine (CuPc) and lead phthalocyanine (PbPc) structures indicate that the angle at which the electromagnetic wave is resonance-absorbed in the structure changes its value with the changing thickness of the phthalocyanine layer. Fig.4 illustrates the dependence of the value of the reflectivity of light on the sensor structure as a function of the angle of incidence of the light in the case of various film thicknesses of copper phthalocyanine CuPc exposed to NO_2 for 30 minutes. As we see in Fig. 4, the values of the detection angle of the plasmon minimum grow with the increasing thickness of the CuPc layer, and the characteristics become deeper, in opposition to lead phthalocyanine (Fig.3).

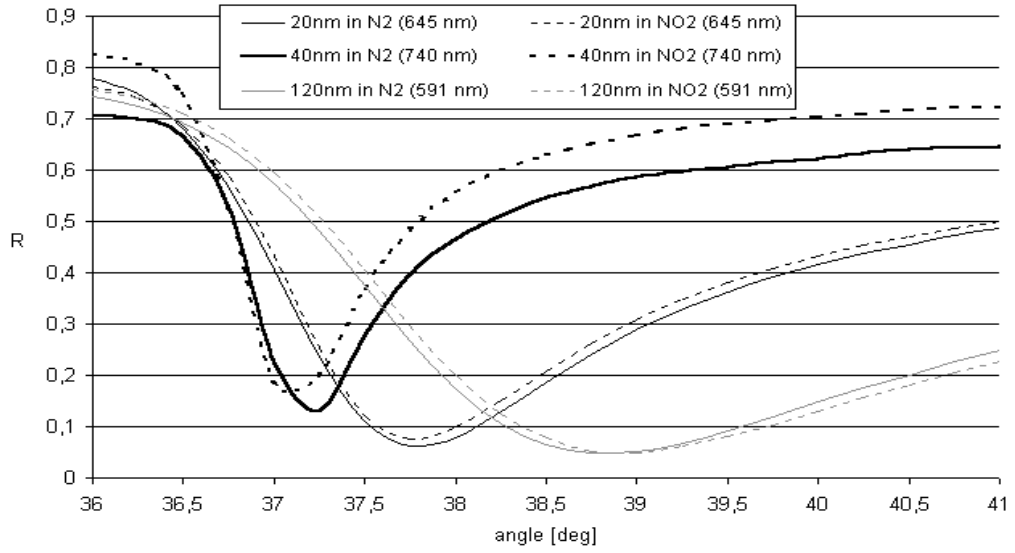

Fig.4 Coefficient of reflection as a function of the detection angle with visible plasmon minima concerning CuPc layers: a) 20nm; b) 40nm; c) 120nm thick, tested in synthetic air and in a mixture of air and 100ppm NO_2

The investigated layers of copper phthalocyanine, 20 to 120nm thick, display a sensitivity to NO_2 over the entire range of wavelengths of visible light. This permits to choose the most

convenient wavelength for which the signal can be detected, selecting the adequate thickness of the phthalocyanine layer in the sensor film structure.

The spectral characteristics of the sensitivity of CuPc layers as a function of the wavelength concerning several thicknesses of these layers can be seen in Fig.5.

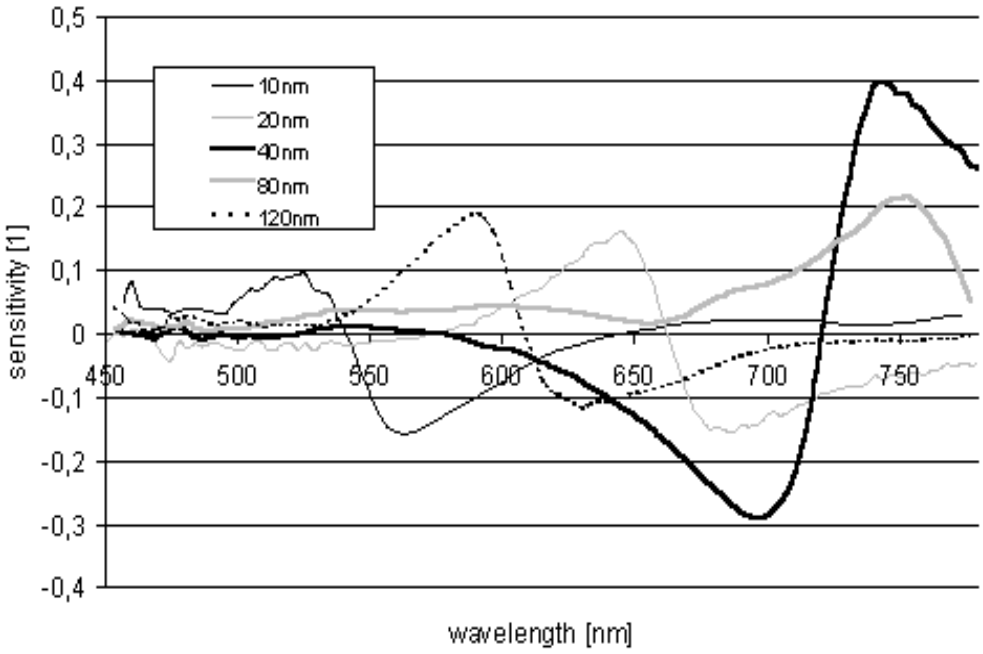

Fig. 5. Spectral characteristics of the sensitivity of sensor layers as a function of the wavelength concerning CuPc layers with a thickness of a) 10nm; b) 20nm; c) 40nm; d) 80nm, e) 120nm.

One might notice, the highest sensitivity is to be found in a cooper phthalocyanine layer 40nm thick at a wavelength of 750nm. Fig.6 shows the sensitivity of a copper phthalocyanine layer exposed to NO_2 as a function of its thickness. Table1 presents a survey of copper phthalocyanine layers, their maximum sensitivities and the angles for which is the maximum sensitivity of detection. Further investigations on copper phthalocyanine were carried out concerning the optimal thickness of 40nm.

2.3 Investigations concerning the regeneration of sensor layers with copper phthalocyanine after their earlier exposed to nitrogen dioxide

The layer of copper phthalocyanine, 40nm thick, was exposed to a mixture of synthetic air and 100ppm NO_2 at a constant flow rate of 1l/min for 30 minutes. Next, this layer was rinsed for 1 hour with synthetic air, keeping up a constant flow rate of the gas. Then layer was left for 21 hours exposed to atmospheric air, after which the structure was submitted to several cycles of exposition to NO_2 and regenerated in synthetic air. Fig. 7 presents the

response of the sensor layer with a CuPc films, exposed in turn to synthetic air and 100ppm NO_2 and again to synthetic air. After the first cycle the layer displayed an almost 100% regeneration in an atmosphere of synthetic air.

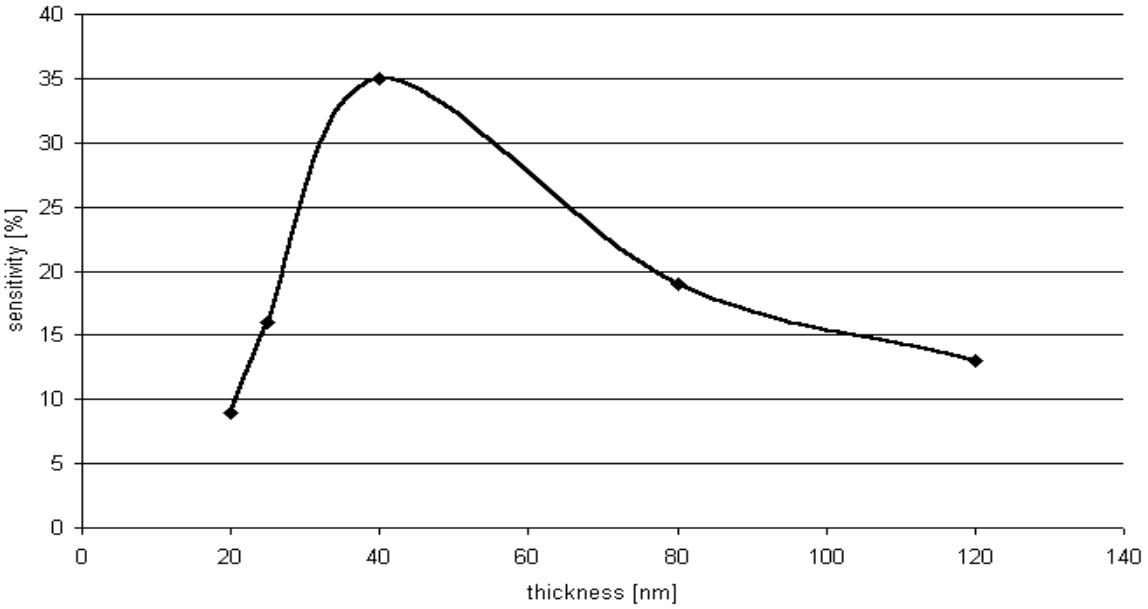

Fig.6 Dependence of the sensitivity of copper phthalocyanine CuPc on the effect of NO_2 as a function of its layer thickness.

Sensor layer	Thickness of the CuPc layer [nm]	Maximum sensitivity [%]	Angle* [degrees]	Wavelength [nm]
1. Au+CuPc	120	19	38,5	591
2. Au+CuPc	80	22	37	750
3. Au+CuPc	40	40	36,75	750
4. Au+CuPc	20	16	37,25	645
5. Au+CuPc	10	9	40,5	525

Table 1. Sensitivities of sensor layers based on gold and copper phthalocyanine when exposed to 100ppm NO_2.

* Angle, at which the sensitivity of the sensor layer reaches its maximum.

Fig.8 contains the dynamic characteristics of the changes in the reflectivity of light from the sensor layer I_R as a function of time concerning four cycles of exposing the sensor layer to nitrogen dioxide with various concentrations. Such an exposition to NO_2 lasted each time about 30 minutes. After each exposition the layer was regenerated for 45 minutes in synthetic air. The arrows in the diagram indicate the consecutive onset and stopping of the

flow of nitrogen dioxide in synthetic air. The investigated CuPc layer, about 40nm thick, does not indicate any marked tendency to regeneration after any one of the cycles, though signal changes when starting the flow of NO_2 and shutting it off are quite distinct. In spite of the lack of a complete regeneration after subsequent cycles of their exposition to NO_2, sensor layers with CuPc are more sensitive to NO_2 in the respective measurement cycles than sensor layers with lead phthalocyanine PbPc [7]. As one see from the examinations, the lead phthalocyanine PbPc and the copper phthalocyanine CuPc may become an interesting sensor material to applied for the NO_2 detection.

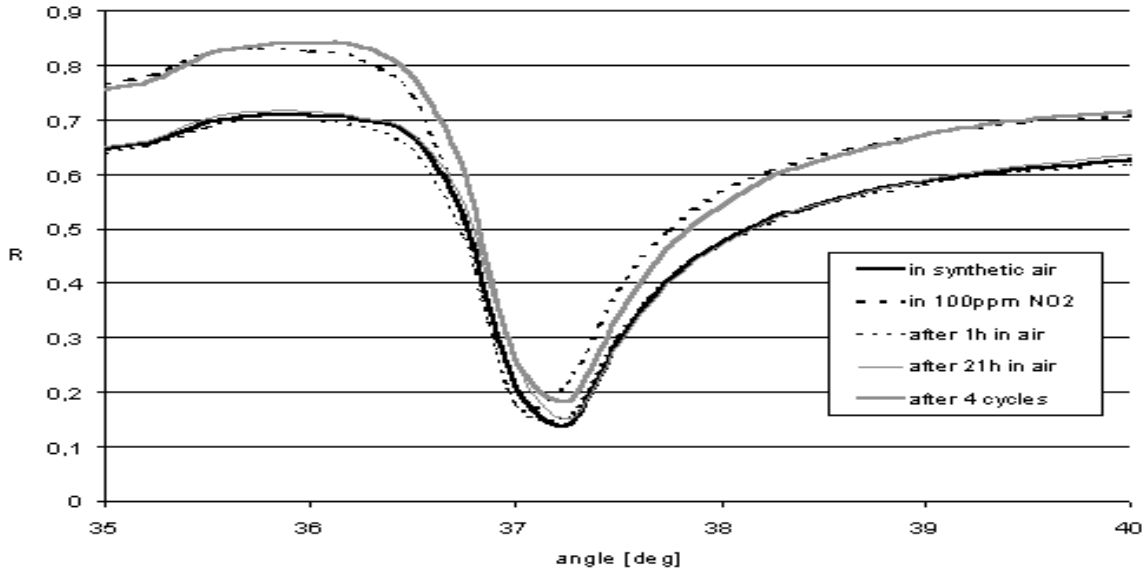

Fig.7 Response of the sensor structure with a 40nm CuPc layer exposed to 100ppm NO_2

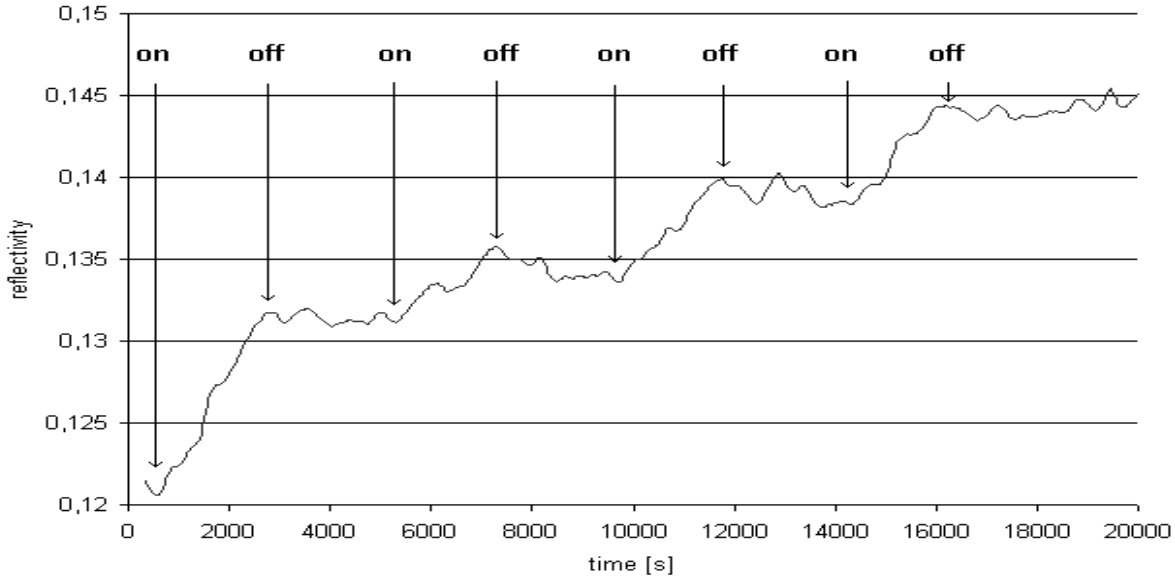

Fig.8 Changes of the reflectivity of light I_R from the sensor layer of 40nm CuPc, cyclically exposed to NO_2 with concentrations of: a) 25ppm; b) 50ppm; c) 75ppm; d) 100ppm in turn with blowing through it synthetic air

Further investigations were carried out in order to explain in which way changes in the technique of depositing thin phthalocyanine films affect their sensor properties.

2.4 Investigations of layers with copper phthalocyanine CuPc deposited by means of vacuum evaporation on a substrate with a temperature of 170°C

For the sake of comparison several sensor layers with copper phthalocyanine deposited on a hot substrate have been investigated. Fig 9 shows the spectral characteristics of the sensitivity of films as a function of the wavelength for thicknesses of CuPc layers ranging from 10 to 80nm. The strongest sensitivity was displayed by a CuPc layer about 30nm thick. Fig. 10 demonstrates the relation of sensitivity as a function of the thickness of CuPc films.

In the case of layer deposited by means of vacuum evaporation on a hot substrate the range of wavelengths is clearly reduced in visible part of the spectrum, in which the layers are sensitive to NO_2. The maximum sensitivity values occur in the red range of the spectrum.

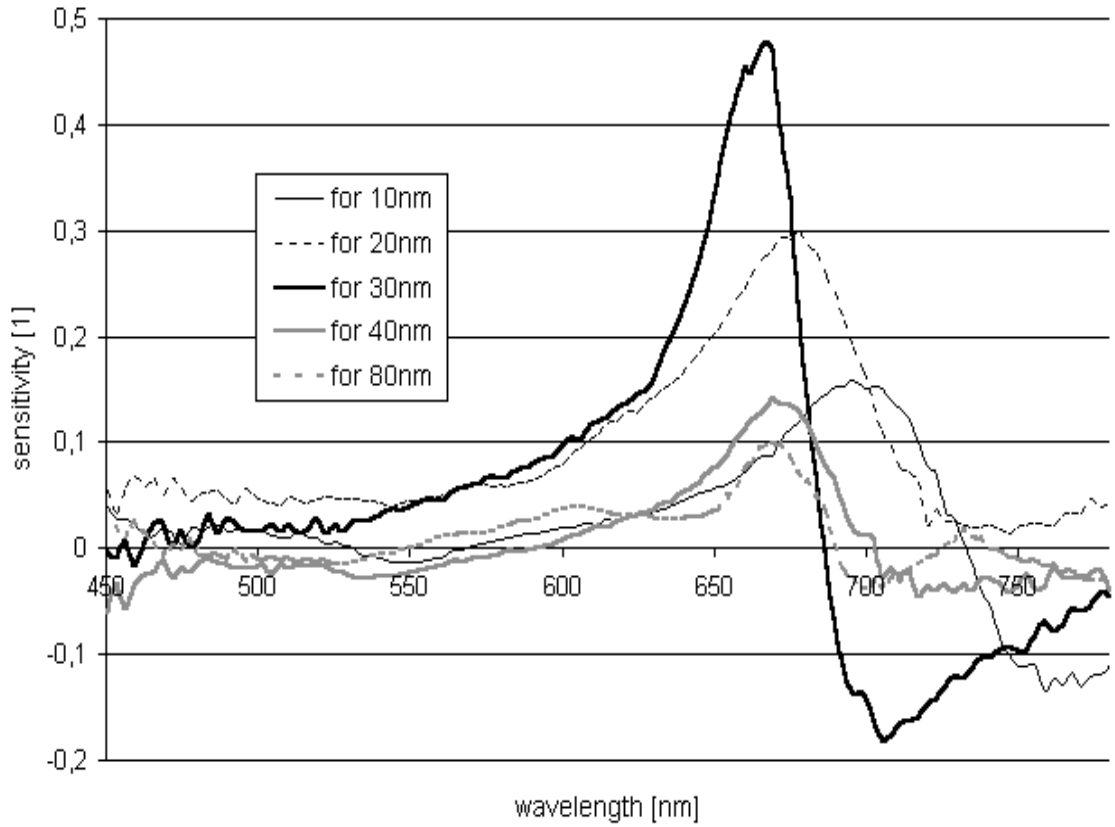

Fig.9 Spectral characteristics of the sensitivity of sensor layers as a function of the wavelength concerning CuPc films with a thickness of: a) 10nm; b) 20nm; c) 30nm; d) 40nm; e) 80nm, deposited on a substrate with a temperature of about 170°C by means of vacuum evaporation.

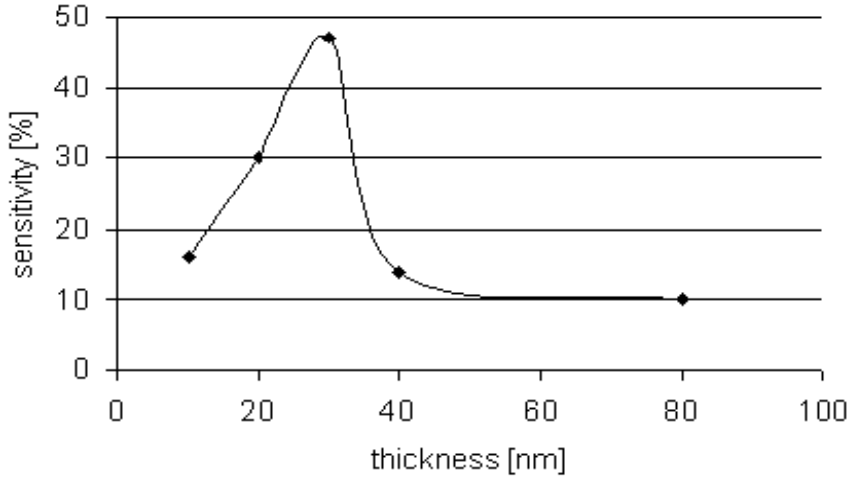

Fig.10 Sensitivity of sensor structures as a function of the thickness of CuPc films deposited on a substrate with a temperature of 170°C

Table 2 provides a review of the investigated layer structures containing CuPc phthalocyanine. These layers did not display any considerable tendencies to regeneration, even after their longer stay (about 20 hours) in synthetic air.

Sensor layer	Thickness of the CuPc layer [nm]	Maximum sensitivity [%]	Angle* [degrees]	Wavelength [nm]
6. Au+CuPc	80	10	37,50	672
7. Au+CuPc	40	14	37,25	672
8. Au+CuPc	30	47	36,25	669
9. Au+CuPc	20	30	37,25	678
10. Au+CuPc	10	16	37,05	696

Table 2. Sensitivities of sensor layers based on gold and copper phthalocyanine deposited on a substrate with a temperature of 170°C, determined when the layers were exposed to 100ppm NO_2

- Angle, at which the sensitivity of the sensor layer reaches its maximum.

3. DISCUSSION AND CONCLUSIONS

Peculiar and various properties of phthalocyanines result from the structure of a macro-ring of phthalocyanine molecule [10]. It is known from literature that phthalocyanines are semiconductors of type p [16, 17] and consequently, they are characterized by acceptor

type of electric conductivity. Adsorption of electron-acceptor gases induces in phthalocyanine generation of charges at shallow acceptor levels. Nitrogen dioxide NO_2 belongs just to the group of electron-acceptor gases. Molecules of phthalocyanines are capable to create coordinate bond together molecules of electron-acceptor gases [17]. Coordinate bond is of the intermediate type between bonds occurring in physical and chemical adsorption. Coordinate bond means that electron doublet comes from one reagent (NO_2) , while the second reagent (MPc) delivers only an electron gap [16]. Coordinate bonds assure higher selectivity of adsorption - for simultaneous action of some gases on phthalocyanine surface the best absorbed is a gas which forms the coordinate bond with phthalocyanine. Thermal gas desorption is facilitated in the case of coordinate bond [17].

The efficiency of surface charge transfer depends on the potential of donor ionisation, acceptor electron affinity and polarization energy resulting form the transfer of anion and positive ion charge transfer (i.e. their energy reaction with a polarized local surrounding) [10]. Gas molecules absorbed on the surface of phthalocyanines which are in the form of solid state have less polarized surrounding than those bound in gaps of porous layers and consequently, they can be easily transferred. It gives a fast surface answer to the influence of NO_2. Gas molecules bound in gaps of a surface give a slow not entirely irrevocable surface answer [10].

The presented investigations comprised an analysis of sensor layers with three phthalocyanines, viz. CuPc and PbPc, deposited on glass substrate with a layer of gold (45nm) at room temperature, elevated temperature (170^{o}C), and also at a temperature reduced to -10^{o}C. The obtained results concerning thin layers of these phthalocyanines (CuPc and PbPc) indicate a distinct relation between the thickness of the layer and its sensitivity. The presented spectral characteristics of the two investigated metal phthalocyanines prove that practically any source of light may be applied in order to detect changes in the properties of Pc layers affected by NO_2 in the plasmon system. In [7] the investigated lead phthalocyanine PbPc layers (deposited on a substrate with room temperature) displayed a dynamic change in the wavelength range in which the phthalocyanine layer is sensitive to NO_2 action, for the changing of the layer thickness within the range 15÷100 nm (Fig.3). Copper phthalocyanine CuPc layers deposited on a substrate at room temperature within the range of thickness of 10nm to 120nm behave analogically. This permits to select the properties of lead and cupper phthalocyanine layers with respect to the required sensitivities. The investigations present an optimisation of the choice of the thickness of copper phthalocyanine layers (Fig.6). In the case of a CuPc layer deposited on a substrate with room temperature, the thickness corresponding to the maximum sensitivity of the layer amounted to 40nm, and in the case of such a layer

deposited on a substrate with a temperature of 170°C this thickness corresponding to 30nm. Investigations on lead phthalocyanine dealt with in [7] have shown that at room temperature of the substrate the optimal thickness of PbPc amounts to 30nm, and at a temperature of 170°C about 40nm.

Investigations concerning the regeneration of the respective layers displayed a differentiated ability to regenerate by rinsing them with nitrogen or synthetic air, depending on the kind of the admixed metallic phthalocyanine and the temperature of the substrate while the sensor layer is being formed. Lead phthalocyanine PbPc layers subjected to NO_2 for about 30 minutes displayed an only insignificant regeneration of their optic properties. Even when they were soaked at a temperature of about 100°C, the properties of PbPc layers did not display any considerable degree of regeneration [7]. For copper phthalocyanine the ability of sensor layers to regenerate is observed already at room temperature (Fig.7).

Basing on the discussed investigations it has been shown that the influence of NO_2 on the tested metalphthalocyanines affects changes of their characteristics and leads to changes of the angle at which the reflection of light from the structure reaches its minimum value. Investigations have also shown, that changes of this angle, caused by NO_2 are, as a rule, not too large, about 2÷3 deg. The influence of NO_2 on the spectral characteristics of metalphthalocyanines becomes evident by changing of the light wavelength, for which changes of the signal brought about by NO_2 reach their maximum, similarly as the changes of the value of this signal. Investigations have proved that the spectral characteristics are extremely sensitive to NO_2 - the position of the signal maximum may change due to the effect of NO_2 even by 200nm. Due to the high sensitivity this way of detection may find practical application in plasmon sensors of NO_2.

It is to be stressed that such versatile experimental investigations on the effect of NO_2 on the sensitivity properties of metalphthalocyanines by means of the plasmon resonance method have not been presented in literature so far. The aim of further investigations is, among others, the determination of the effect of NO_2 adsorption on the optical properties of a lamellas structure - the coefficient of reflection, the absorption coefficient, and - first of all, the effective index of refraction. The results of investigations gathered so far are extremely interesting and will be published in the nearest future.

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REFERENCES

1. J. Ignac-Nowicka, *"Air polution monitoring at the workstand and in the ambient air", Molecular and Qantum Acoustics*, vol **22**, 113-121, (2001)
2. J. Ignac-Nowicka, T. Pustelny, "Monitoring methods of nitrogen dioxide", *Molecular and Qantum Acoustics*, vol **22**, 171-182, (2001)
3. G.J. Ashwell, M.P.S. Roberts, "Highly selective surface plasmon resonance sensor for NO_2", *Electronics Letters*, Vol. **32**, No.22, 2089-2091, (1996).
4. E. Maciak, A. Opilski, Z. Opilski, "Surface plasmon resonance liquid sensor based on prism coupler in the Kretschmann geometry", *Molecular and Quantum Acoustics*, Vol. **21**, 173-178, (2000).
5. E. Maciak, Z. Opilski, T. Pustelny, J. Ignac-Nowicka, "Examination of thin films of phthalocyanines from the point of view of their application in NO_2 sensors*", Molecular and Qantum Acoustics*, vol **23**, 253-269, (2002).
6. J. Homola, S.S. Yee, G. Gauglitz, "Surface plazmon resonance sensors: review", *Sensors and Actuators,* B **54**, 3-15, (1999).
7. J. Ignac-Nowicka, T. Pustelny, E. Maciak, Z. Opilski, W. Jakubik, M. Urbańczyk, "Examination of thin films of phthalocyanines in plasmon system for their application in NO_2 sensor", *Optical Enginering*, vol. **42**, No. 10, 1-9, (2003).
8. B. Schollhorn, J.P. Germain, A. Pauly, C. Maleysson, J.P. Blanc, "Influence of peripheral electron-withdrawing substitutents on the conductivity of zinc phtalocyanine in the presence of gases. Part 1: reducing gases", *Thin Solid Films,* **326**, 245-250, (1998).
9. D. Campbell, R.A. Collins, "A study of the interaction between nitrogen dioxide and lead phthalocyanine using electrical conduction and optical absorption", *Thin Solid Films*, **295**, 277-282, (1997).
10. A. Mrwa, M. Friedrich, A. Hofmann, D.R.T. Zahn, "Response of lead phthalocyanine to high NO2 concentration"*, Sensors and Actuators* B, **24-25**, 596-599 (1995).
11. J. D. Wright, A. Cado, S. J. Peacock, V. Rivalle, A. M. Smith, "Effects of nitrogen dioxide on surface plasmon resonance of substituted phthalocyanine films" ,*Sensors and Actuators* B, **29**, 108-114, (1995).
12. R.A. Collins, M.K.Ellis, T.A.Jones, "Sensitivity of lead phtalocyanine thin films to ammonia and nitrogen dioxide", *Chemtronics*, vol.**5**, 93-95, (1991).
13. T. Pustelny, B. Pustelny, "Investigation of electroluminophores for their practical application in fiber sensor technology", *OPTO-ELECTRONICS Review*, 10(3), 123-128, (2002).
14. Y.H. Ju, C. Hsieh, C.J. Liu, "The surface reaction and diffusion of NO_2 in lead phthalocyanine thin film", *Thin Solid Films,* **342**, 238-243, (1999).
15. E. Kretschmann, "The Determination of the Optical Constant of Metals by Excitation of Surface Plasmons", *Z. Physik*, **241**, 313-324, (1971).
16. W. Gopel, K.D. Schirbaum, D.Schmeisser , "Prototype chemical sensors for the selective detection of O_2 and NO_2 in gases"*, Sensors and Actuators* **17**, 377-384, (1989)

17. H. Mockert, D.Schmeisser, W. Gopel , “Lead phthalocyanine (PbPc) as a prototype organic material for gas sensors: comparative electrical and spectroscopic studies to optimise O_2 and NO_2 sensing”,. *Sensors and Actuators* **19**, 159-176, (1989)

18. T. Pustelny, J. Ignac-Nowicka, Z. Opilski, Experimental Investigations of Thin Metalphthalocyanine Layers CuPc, PbPc, NiPc by Plasmon Resonance Method to Be Applied in NO_2 - *Sensors, Optica Applicata, will be published*