

# **Experimental investigation of thin metalphthalocyanine layers CuPc, PbPc, NiPc by plasmon resonance method to be applied in NO<sub>2</sub>-sensors**

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The surface plasmon resonance spectroscopy is an optical 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, lead and nickel phthalocyanines have been examined in the plasmon system from the point of view of their application to NO<sub>2</sub> sensors.

Keywords: surface plasmon resonance, dioxide nitrogen detection, phthalocyanine.

## **1. Introduction**

Industrial activities and the development of urban agglomerations have resulted in the occurrence of quite a number of chemical substances in the air, including gaseous substances such 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 sensing layer brought about by changes in the

concentration of ambient gases. These changes are recorded by means of the surface plasmon resonance (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 maintain at the metal-dielectric as well as metal-semiconductor interlayer, when an electromagnetic wave strikes the surface. The idea of the plasmon sensor operation consists in the equalization of the propagation constants of the plasmon wave  $\beta_{\text{SPW}}$  and the propagation constant of the electromagnetic optical wave  $\beta_{\text{e-m}}$  [6]. Therefore, the exciting electromagnetic wave is directed towards the interlayer of these two media through some material with a higher refractive index (*e.g.*, glass, plastics) at an adequate angle  $\theta(\lambda)$ , characteristic of a 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 medium investigated can be detected by analysing the intensity of the optical wave, which interacts with the surface plasmon wave (SPW).

Based on our previous investigations and on references found in literature [5]–[14], it results that molecular crystals, to which metallic phthalocyanines belong, display high sensitivity to oxidizing and reductive gases, including  $\text{NO}_2$ . 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 characteristics, 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  $\text{NO}_2$ -atmosphere. Such investigations were carried out at  $\text{NO}_2$ -concentrations of 100 ppm in nitrogen for three different metallic phthalocyanines, *viz.* copper, nickel and lead phthalocyanines, with differing their film thicknesses and different conditions of their deposition.

## 2. Experimental investigation

### 2.1. Idea of measurements and diagram of the measuring stand

In this investigation an optical measurement system was applied based on Kretschmann's idea of such a system [15]. The sample in the form of a thin-layer sensor structure (Fig. 1) is placed on a goniometric table. On one side the sample is coupled with a prism, on the other with a chamber into which gases of known composition are pumped. The gases were batched by means of a coupled computer of programmer mixing the gases. With gases flowing through the chamber at a rate of  $1 \text{ dm}^3/\text{min}$ , the  $\text{NO}_2$ -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 structure is irradiated by the white light. The light going through the optical fiber, strikes on the prism where it is reflected from the surface of the sensor

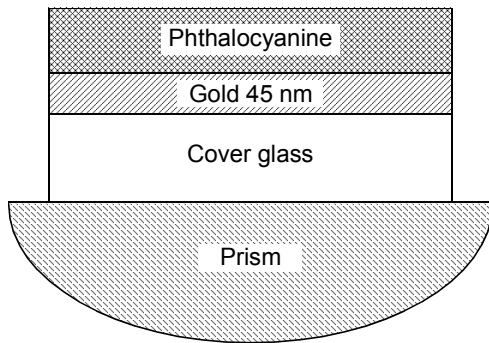


Fig. 1. Lamellar structure with a sensor layer of phthalocyanine.

and enters a photodetector. The signal goes parallel to the photodetector and to the spectrometer and next it is recorded by the computer. The idea of the test stand is depicted in Fig. 2. A detailed description of such a measuring stand and its diagram in [5], [7] have been presented.

Thanks to the application of goniometer (controlled by a computer), this measuring system permits us to measure simultaneously the signal values on the photodetector as a function of the wavelength and the function of the angle between the sample and the light wave vector for the whole light spectrum during the same measurement series. The application of a spectrometer (WCad 3 type) permits us to measure the signal over the whole spectrum of visible light. The numerical program, developed for the purpose of analysing the results obtained, makes 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 investigation of lead phthalocyanines were presented in [7]. The present paper deals with the sensitivity of sensor structures with copper, nickel

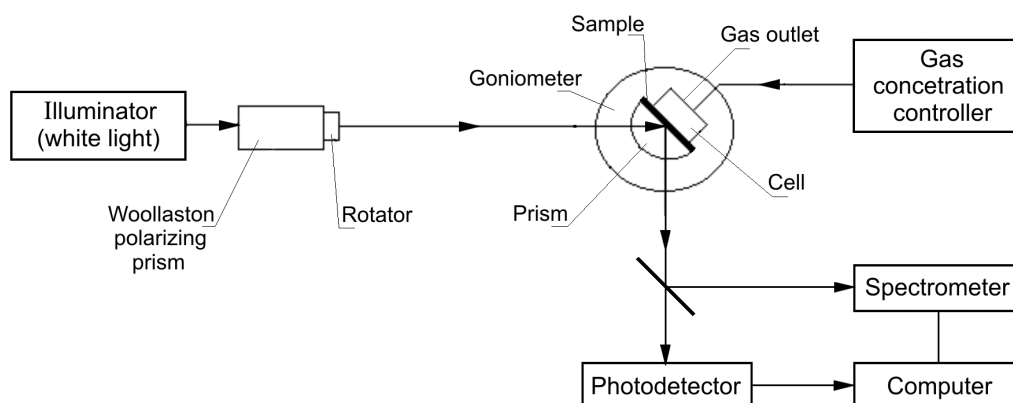


Fig. 2. Diagram of the measuring stand.

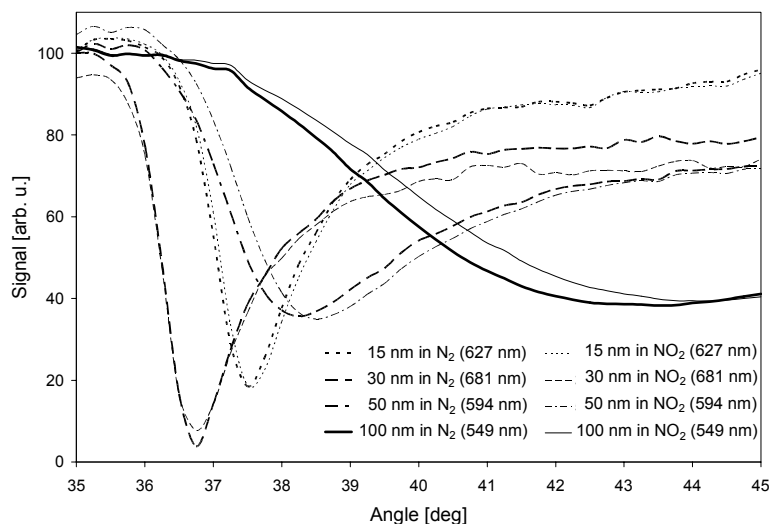


Fig. 3. Signal in the detector as a function of the detection angle with visible plasmon minima in the case of PbPc (15, 30, 50 and 100 nm thick), tested in  $N_2$ , and in the mixture of  $N_2$  and 100 ppm  $NO_2$ .

and lead phthalocyanines to  $NO_2$  actions. The sensitivity of the structure to  $NO_2$  is defined as:

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

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 concentration tested.

The theoretical analysis presented in [6] indicates that the spectral characteristics obtained from the 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 a given sensor layer, the most intensive resonance absorption of the electromagnetic energy of the wave striking the structure occurs in favour of the surface plasmon wave [3]–[6]. According to investigation presented in [7] the angle at which resonance absorption of the electromagnetic wave occurs, changes its value with a change of phthalocyanine film thickness in the lamellar structure of the sensor. Figure 3 presents the results obtained concerning lead phthalocyanine.

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

Sensor structures were used in the experiments, consisting of a layer of gold and copper phthalocyanine deposited on a glass substrate by means of vacuum evaporation.

The temperature of the substrate was about 27 °C (300 K). The gold layer was 45 nm thick, the thicknesses of phthalocyanines were from 10 to 120 nm range. Phthalocyanine were deposited by vacuum evaporation using predetermined rated characteristic of evaporation at 300 °C [7]. Processes of the technological production of phthalocyanine sensor structures are presented in detail in [15], [16].

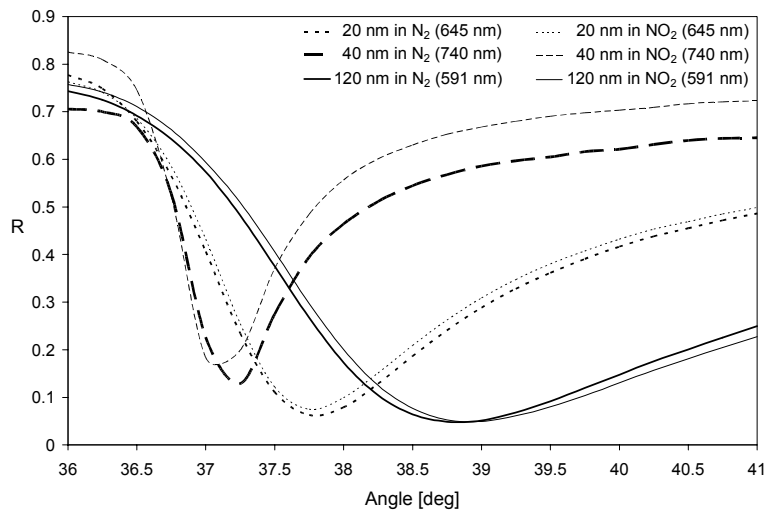


Fig. 4. Coefficient of reflection as a function of the detection angle with visible plasmon minima concerning CuPc layers (20 nm, 40 nm and 120 nm thick), tested in synthetic air and in a mixture of air and 100 ppm NO<sub>2</sub>.

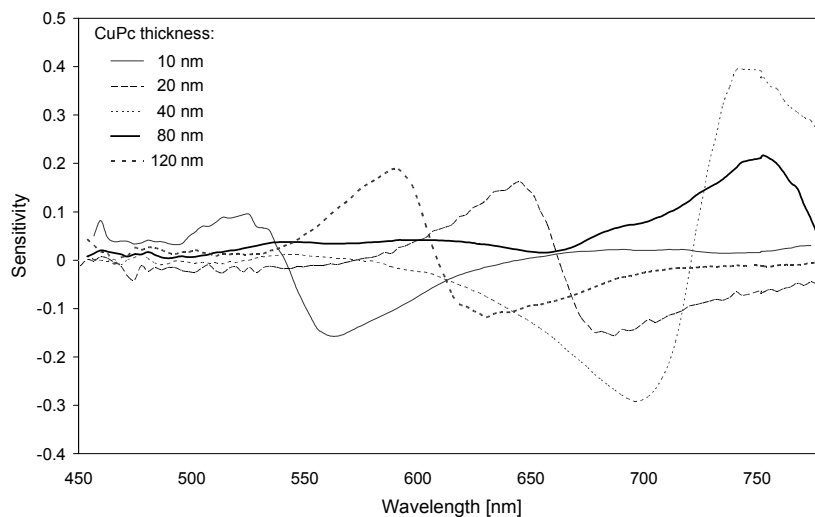


Fig. 5. Spectral characteristics of the sensitivity of sensor layers as a function of the wavelength concerning CuPc layers.

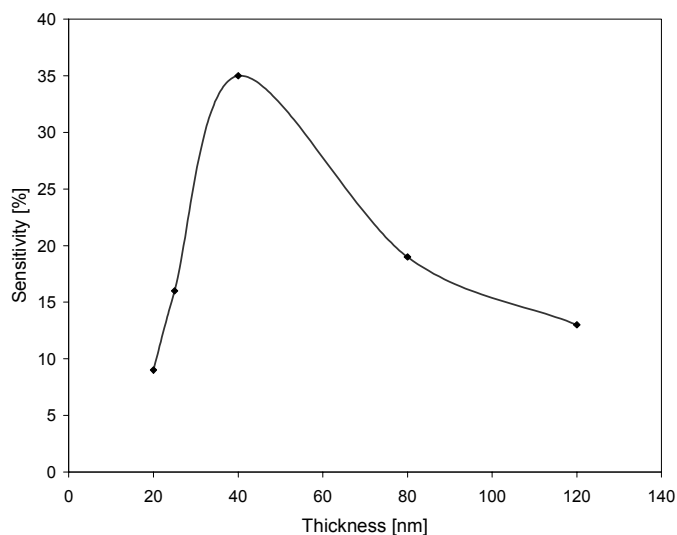


Fig. 6. Dependence of the sensitivity of copper phthalocyanine CuPc on the effect of  $\text{NO}_2$  as a function of its layer thickness.

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 changing thickness of the phthalocyanine layer. Figure 4 illustrates the dependence of the value of light reflectivity 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  $\text{NO}_2$  for 30 minutes. As can be seen from Fig. 4, values of the detection angle of the plasmon minimum grow with an increasing thickness of the CuPc layer, and the characteristics become deeper, in opposition to lead phthalocyanine (Fig. 3).

The layers of copper phthalocyanine, 20 to 120 nm thick, display sensitivity to  $\text{NO}_2$  over the entire range of wavelengths of visible light. This permits us to choose

Table 1. Sensitivities of sensor layers based on gold and copper phthalocyanine when exposed to 100 ppm  $\text{NO}_2$ .

Sensor layer	Thickness of the CuPc layer [nm]	Maximum sensitivity [%]	Angle* [deg]	Wavelength [nm]
Au + CuPc	120	19	38.5	591
Au + CuPc	80	22	37	750
Au + CuPc	40	40	36.75	750
Au + CuPc	20	16	37.25	645
Au + CuPc	10	9	40.5	525

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

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. One might notice that the highest sensitivity is to be found in a copper phthalocyanine layer 40 nm thick at a wavelength of 750 nm.

Figure 6 shows the sensitivity of a copper phthalocyanine layer exposed to  $\text{NO}_2$  as a function of its thickness. Table 1 presents a survey of copper phthalocyanine layers, their maximum sensitivities and angle for which the sensitivity of detection is maximal. Further investigation on copper phthalocyanine was carried out concerning the optimal thickness of 40 nm.

### 2.3. Investigation concerning the regeneration of sensor layers with copper phthalocyanine after their earlier exposition to nitrogen dioxide

The layer of copper phthalocyanine, 40 nm thick, was exposed to a mixture of synthetic air and 100 ppm  $\text{NO}_2$  at a constant flow rate of  $1 \text{ dm}^3/\text{min}$  for 30 minutes. Next, this layer was rinsed for 1 hour with synthetic air, keeping up a constant flow rate of the gas. Then the layer was exposed to atmospheric air for 21 hours, after which the structure was submitted to several cycles of exposition to  $\text{NO}_2$  and regenerated in synthetic air.

Figure 7 presents the response of the sensor layer with a CuPc film, exposed in turn to synthetic air and 100 ppm  $\text{NO}_2$  and again to synthetic air. After the first cycle the layer displayed an almost 100% regeneration in synthetic air.

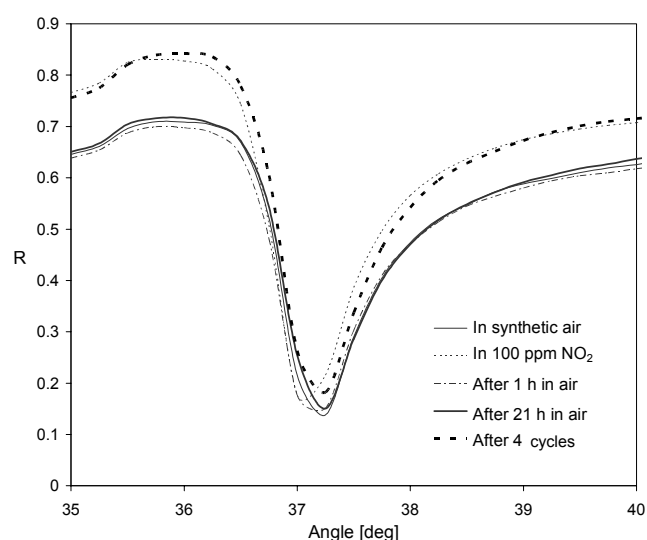


Fig. 7. Response of the sensor structure with a 40 nm CuPc layer exposed to 100 ppm  $\text{NO}_2$ .

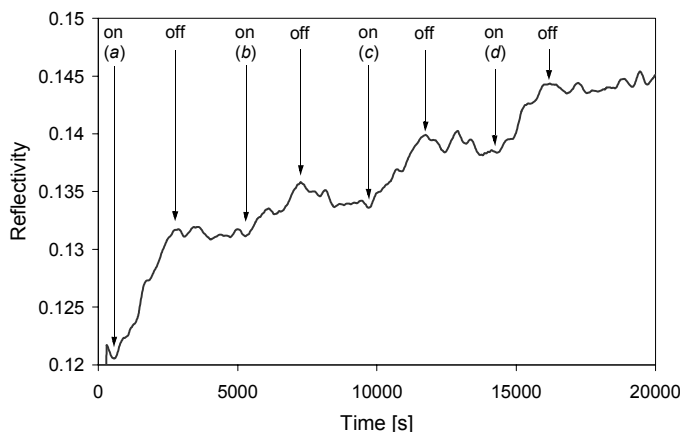


Fig. 8. Changes of the reflectivity of light  $I_R$  from the sensor layer of 40 nm CuPc, cyclically exposed to  $\text{NO}_2$  with concentrations of: 25 ppm (a), 50 ppm (b), 75 ppm (c), 100 ppm (d) in turn with synthetic air blowing through it.

Figure 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 of various concentrations. Such an exposition to  $\text{NO}_2$  lasted about 30 minutes each time. 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 CuPc layer, about 40 nm thick, does not indicate any marked tendency towards regeneration after any one of the cycles, though signal changes when starting the flow of  $\text{NO}_2$  and shutting it off are quite distinct. Although there is no complete regeneration after subsequent cycles of exposition to  $\text{NO}_2$ , sensor layers with CuPc are more sensitive to  $\text{NO}_2$  in the respective measurement cycles than sensor layers with lead phthalocyanine PbPc [7]. As one can see from the examinations, the lead phthalocyanine PbPc and the copper phthalocyanine CuPc may become an interesting sensor material to be applied for the  $\text{NO}_2$  detection.

Further investigation was carried out in order to explain in what way changes in the technique of depositing thin phthalocyanine films affect their sensor properties.

#### 2.4. Investigation 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. Figure 9 shows the spectral characteristics of the sensitivity of films as a function of the wavelength for thicknesses of CuPc layers



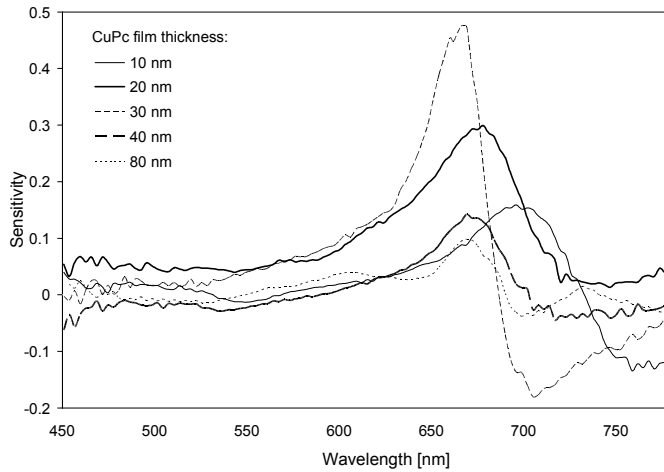


Fig. 9. Spectral characteristics of the sensitivity of sensor layers as a function of the wavelength concerning CuPc films (10, 20, 30, 40 and 80 nm thick) deposited on a substrate with a temperature of about 170 °C by means of vacuum evaporation.

ranging from 10 to 80 nm. The strongest sensitivity was displayed by a CuPc layer about 30 nm thick. Figure 10 demonstrates the sensitivity of the structures as a function of the thickness of CuPc films. In the case of layers deposited by means of vacuum evaporation on a hot substrate the range of wavelengths in visible part of the spectrum, in which the layers are sensitive to NO<sub>2</sub>. The maximum sensitivity values occur in the red range of the spectrum.

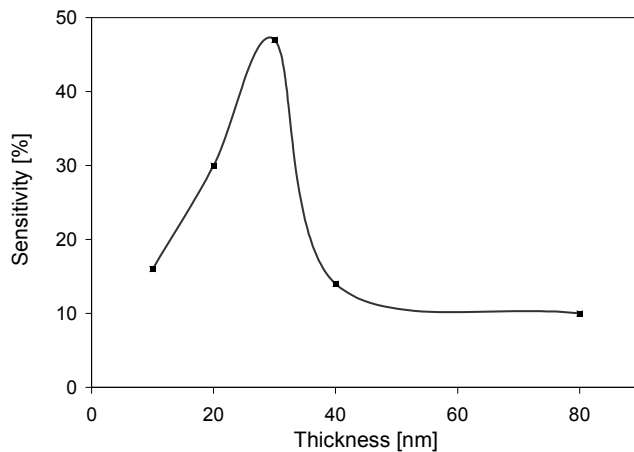


Fig. 10. Sensitivity of sensor structures as a function of the thickness of CuPc films deposited on a substrate with a temperature of 170 °C.

Table 2. 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 100 ppm NO<sub>2</sub>.

Sensor layer	Thickness of the CuPc layer [nm]	Maximum sensitivity [%]	Angle* [deg]	Wavelength [nm]
Au + CuPc	80	10	37.50	672
Au + CuPc	40	14	37.25	672
Au + CuPc	30	47	36.25	669
Au + CuPc	20	30	37.25	678
Au + CuPc	10	16	37.05	696

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

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

### 2.5. Response of a sensor layer with nickel phthalocyanine NiPc deposited on gold substrate after its stay in nitrogen dioxide

The nickel phthalocyanine layers were deposited by means of vaporization on a glass substrate covered with a layer of gold 40 nm thick at 30 °C (~300 K). Figure 11 presents the plasmon minima of several lamellar structures with nickel phthalocyanine. The respective pairs of characteristics corresponding to the layers investigated, presented in Fig. 11, concern wavelengths for which the sensitivity of the layer

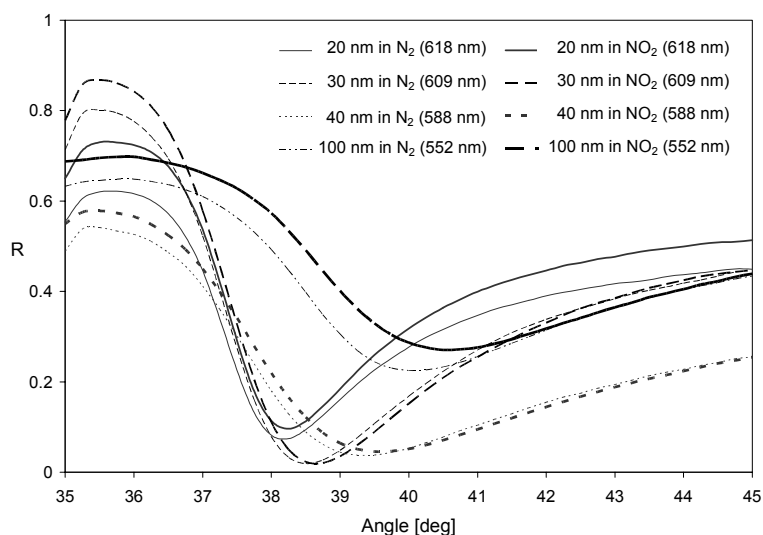


Fig. 11. Characteristics of the reflection coefficient as a function of detection angle with plasmon minima of NiPc layers (with thicknesses of: 20 nm, 30 nm, 40 nm, 100 nm) tested in N<sub>2</sub> and a mixture of N<sub>2</sub> and 100 ppm NO<sub>2</sub>.

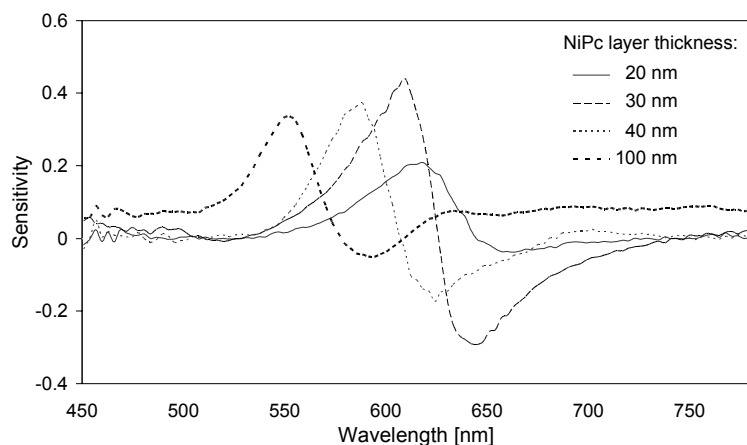


Fig. 12. Sensitivity of the NiPc structure (20, 30, 40 and 100 nm thick) as a function of the wavelength.

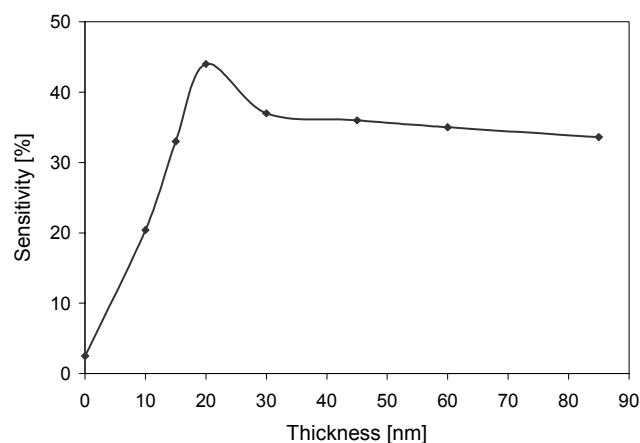


Fig. 13. Sensitivity of NiPc structure as a function of its film thickness.

examined displayed its maximum. As one can see, the sensitivity depends on a change in position of the resonance curve obtained during the exposition to  $\text{NO}_2$  with regard to a characteristic obtained during the exposition to  $\text{N}_2$ . In the case of a layer about 30 nm thick the lowest plasmon minimum was observed, which points to this layer as being the most sensitive. The sensitivity recorded for this structure amounts to about 45% at a resonance angle of  $38.25^\circ$  and a wavelength of 609 nm. Nickel phthalocyanine layers vaporized on a glass substrate at room temperature display sensitivity within a narrow range of 530–630 nm, *i.e.*, practically in the range of yellowish-orange light.

Figure 12 shows the dependence of sensitivity of a NiPc structure as a function of the wavelength of light concerning NiPc layers with a thickness of 20–100 nm.

The sensitivity of selected layers of nickel phthalocyanine as a function of their thickness is shown in Fig. 13.

### 2.6. Investigation of the regeneration of sensor layers with nickel phthalocyanine NiPc deposited on glass substrate at room temperature

The sensor structure with nickel phthalocyanine, about 30 nm thick, was exposed repeatedly to nitrogen dioxide with a concentration of 100 ppm in nitrogen. Figure 14 presents the subsequent positions of the plasmon minima as a relation between the coefficient of reflection  $R$  and the detection angle of a beam reflected from the surface of the sensor. The sensor layer of the sample was successively subjected for half an hour to the effect of nitrogen and nitrogen dioxide (100 ppm) and next for one hour to  $N_2$  only, and again for half an hour to  $NO_2$ . After one hour of rinsing with  $N_2$ , no

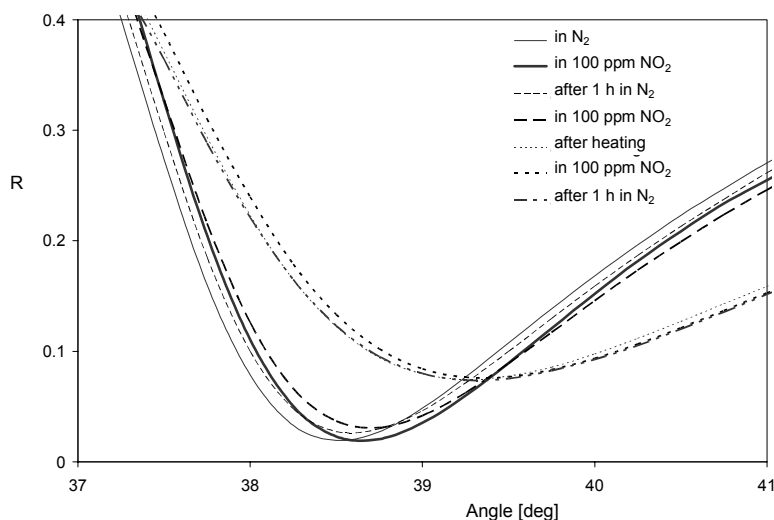


Fig. 14. Dependence of the reflection coefficient on the detection angle for the exposure of the structure on  $NO_2$  and after its regeneration in  $N_2$ .

complete regeneration was observed, but each successive exposition of the layer to  $NO_2$  resulted in the same change in response of the sensor layer as during the first exposition to  $NO_2$ , whereas the sensitivity value remained unchanged. Then this structure was soaked for two hours in vacuum at a temperature of  $80\text{ }^\circ\text{C}$ , and again exposed to 100 ppm  $NO_2$  and regenerated for 1 hour in  $N_2$ . After soaking the layer was less sensitive to  $NO_2$ , but regenerated to a greater extent than before the soaking (Fig. 14).

### 2.7. Investigation of sensor layers with nickel phthalocyanine deposited on the glass substrate at a temperature of $-10\text{ }^\circ\text{C}$

The sensor layers were deposited on the glass substrate by means of vacuum vaporization but the layer of gold was deposited at room temperature, after which the

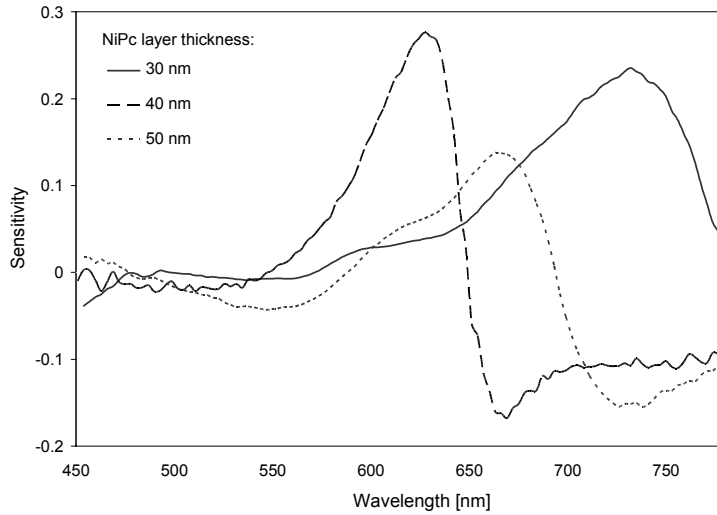


Fig. 15. Sensitivity of sensor layers with NiPc deposited on a substrate with a temperature of  $-10\text{ }^{\circ}\text{C}$  as a function of wavelength.

NiPc layer was put on the substrate which had been cooled down to  $-10\text{ }^{\circ}\text{C}$ . The substrate was cooled in vacuum chamber, applying Peltier’s pile. Figure 15 presents the sensitivities of sensor layers obtained in the way described above with various thicknesses of NiPc structure.

From among the three layers investigated the 40 nm film displayed the highest sensitivity. For the thickness of 627 nm and a detection angle of  $38^{\circ}$  the sensitivity

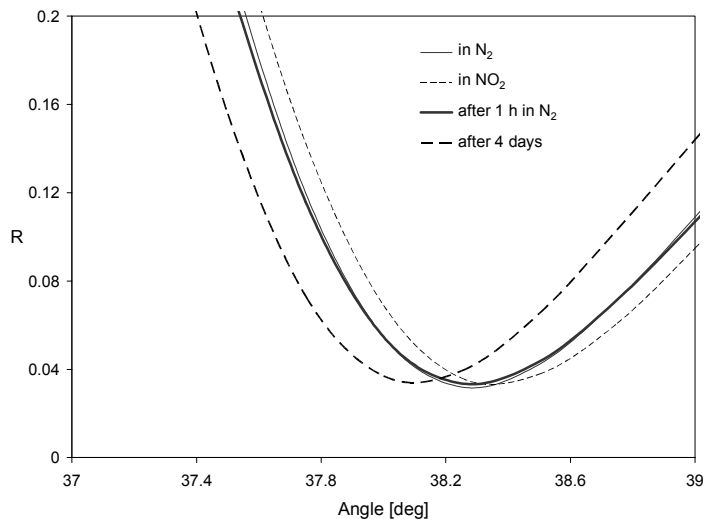


Fig. 16. Dependence of the coefficient of reflection on the detection angle during the exposition of a sensor layer with 40 nm NiPc to  $\text{N}_2$  and 100 ppm  $\text{NO}_2$ .

amounted to 28%. Next the sensor structure with a NiPc layer of 40 nm was subjected to special investigation in order to determine the degree of regeneration of the layer after earlier exposition to NO<sub>2</sub>. After half an hour's exposition to NO<sub>2</sub> the sensor layer was rinsed and displayed a nearly full regeneration. Other characteristics obtained as a result of this experiment may be gathered from Fig. 16.

### 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* [17], [18] 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<sub>2</sub> belongs just to the group of electron-acceptor gases. Molecules of phthalocyanines are capable of creating a coordinate bond together with molecules of electron-acceptor gases [18]. The coordinate bond is of the intermediate type between bonds occurring in physical and chemical adsorption. The coordinate bond means that electron doublet comes from one reagent (NO<sub>2</sub>), while the second reagent (MPC) delivers only an electron gap [17]. Coordinate bonds assure higher selectivity of adsorption – for simultaneous action of some gases on phthalocyanine surface the best absorbed is a gas which forms a coordinate bond with phthalocyanine. Thermal gas desorption is facilitated in the case of coordinate bond [18].

The efficiency of surface charge transfer depends on the potential of donor ionisation, acceptor electron affinity and polarization energy resulting from the transfer of anion and positive ion charge transfer (*i.e.*, their energy reaction with polarized local surroundings) [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. This gives a fast surface response to the influence of NO<sub>2</sub>. Gas molecules bound in gaps of a surface give a slow not entirely irrevocable surface response [10].

The investigation presented comprised an analysis of sensor layers with three phthalocyanines, viz. CuPc, NiPc, PbPc, deposited on glass substrate with a layer of gold (45 nm) at room temperature, elevated temperature (170 °C), and also at a temperature reduced to –10 °C. The results obtained concerning thin layers of these phthalocyanines (CuPc, NiPc and PbPc) indicate a distinct relation between the thickness of the layer and its sensitivity. The spectral characteristics of the three 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<sub>2</sub> in the plasmon system. In [7] the 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<sub>2</sub> action, for the layer thickness changing within the range 15–100 nm (Fig. 3). Copper phthalocyanine CuPc layers deposited on a substrate at room temperature within the range of thickness from 10 to 120 nm behave

in the same way. This permits us to select the properties of lead, copper and nickel phthalocyanine layers with respect to the required sensitivities. Layers of the nickel phthalocyanine displayed a reduced range of maximum sensitivities from 525 to 625 nm in the phthalocyanine thickness range from 20 to 100 nm. These layers were deposited on a substrate with room temperature. As we can see from Fig. 12, in such a case the possibility of selecting the proper wavelength of light required to detect changes in the sensor layer is rather limited. The investigation presents 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 40 nm, and in the case of such a layer deposited on a substrate with a temperature of 170 °C this thickness amounted to 30 nm. Investigation of lead phthalocyanine dealt with in [7] has shown that at room temperature of the substrate the optimal thickness of PbPc amounts to 30 nm, and at a temperature of 170 °C to about 40 nm. A different dependence was found in the case of nickel phthalocyanine. Here the optimal thickness of the layer amounts to 30 nm for the substrate of room temperature and to about 40 nm when the substrate was cooled down to -10 °C.

Investigation 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<sub>2</sub> for about 30 minutes displayed 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). The best regeneration of a phthalocyanine layer which had absorbed nitrogen dioxide on its surface could be observed in the case of a nickel phthalocyanine layer, 40 nm thick, deposited on a substrate with the temperature -10 °C. It ought, however, to be mentioned that a sensor layer deposited on a cooled substrate (-10 °C) is characterized by the least mechanical resistance among all the layers investigated.

Based on the investigations discussed it has been shown that the influence of NO<sub>2</sub> on the 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<sub>2</sub> are, as a rule, not too large, about 2–3 deg. The influence of NO<sub>2</sub> on the spectral characteristics of metalphthalocyanines becomes evident when changing the light wavelength, for which changes of the signal brought about by NO<sub>2</sub> 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<sub>2</sub> – the position of the signal maximum may change due to the effect of NO<sub>2</sub> even by 200 nm. Due to the high sensitivity this way of detection may find practical application in plasmon sensors of NO<sub>2</sub>.

It is to be stressed that such versatile experimental investigation into the effect of NO<sub>2</sub> on the sensitivity properties of metalphthalocyanines by means of the plasmon resonance method has not been presented in literature so far. The aim of further investigation is, among others, the determination of the effect of NO<sub>2</sub> adsorption on the optical properties of a layered 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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