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Optical investigations on layered metalphthalocyanine nanostructures affected by NO_2 applying the surface plasmon resonance method

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The paper deals with investigations concerning the optical parameters of the layers of selected phthalocyanines by means of the surface plasmon resonance method. The values of the refracting index and the coefficient of extinction for copper and lead phthalocyanines have been determined. The presented results concern the layers occurring in the surrounding atmospheric air before and after exposure to 100 ppm nitrogen dioxide. The obtained dispersive characteristics were determined ellipsometrically and using the surface plasmon resonance method, by adapting theoretical relations to the experimental dependence of the surface plasmon resonance. The resulting values of the complex refracting index for the tested phthalocyanines were compared with the values obtained by ellipsometric measurements.

Keywords: metalphthalocyanines, dispersion of refractive index, nitrogen dioxide, surface plasmon resonance.

1. Introduction

The technical development of devices monitoring the air aims at the designing of such devices which might be widely applied in industrial metrology. New methods of detecting the presence of gases have been described in literature all over the world and provide numerous technical solutions, among which the adequate technique of producing elements for sensors is the main issue of investigations. The development of gas sensors aims towards the search for new materials meeting the requirements of a high sensitivity and selectivity of a gas sensor. The problem of designing reliable chemical sensors detecting variations in the presence of toxic gases belongs to the most important tasks of contemporary ecology. This determines the necessity of intensive researches and investigations concerning the physico-chemical properties of already known compounds and syntheses of new substances.

In recent years more and more investigations have been devoted to studies concerning the electrophysical and sorption properties of phthalocyanine (Pc), *i.e.*, compounds with a wide range of applications in chemical sensors used in the analysis of gases [1]–[5]. The present paper deals with the dispersive characteristics of the complex refraction index of thin phthalocyanine layers in the atmospheric air. The dispersive characteristics of the real and imaginary part of the refraction index were determined by means of the surface plasmon resonance method, adapting the theoretical results to the experimental dependence of the phenomenon of the surface plasmon resonance. Moreover, the effect of nitrogen dioxide on the dispersive characteristics of the refraction index of copper and lead phthalocyanine layers has been tested. The obtained values were verified ellipsometrically for a wavelength of 633 nm.

2. Experimental investigations

Series of measurements of the reflectivity of light from a thin-layered structure has been carried out in the presence of the phenomenon of surface plasmon resonance. The physical fundamentals of this phenomenon and its application have been dealt with in [2], [3], [6]. In our investigations we applied an optical system of measurements based on the idea of Kretschmann's system, which is well known from literature [2], [6], [7]. The tested specimen, being a thin-layered NO_2 sensor structure (Fig. 1), was placed on a goniometric table. On one side it was coupled with a prism, on the other with a chamber, into which gases of a known composition were pumped. The gases were batched into the test chamber by means of a mass flow controller (MFC) coupled with a computer. At a gas flow of 1 liter/min through the test chamber, the NO_2 concentration was controlled with an accuracy of about 0.5 ppm. The tested plasmon structure is illuminated from a source of white light. Through an optical fiber and

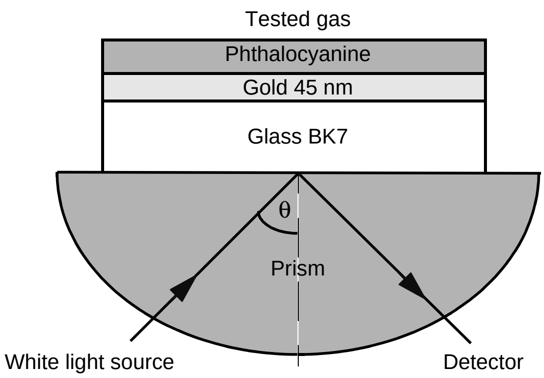

Fig. 1. Layer structure with a phthalocyanine.

polarizer this light strikes the prism, is reflected from the surface of the sensor structure and passes into a detector. The signal from the detector is directed towards the spectrometer and recorded by the computer. A detailed description of the measuring stand and its diagram may be found in [3], [4]. Thanks to the application of the computer-aided goniometric table this system of measurements permits to measure at the same time the signal on the detector as a function of the wavelength and in the function of the position angle of the sample in relation to the light beam for a selected wavelength in one series of measurements. The measuring stand permits to measure the signal from the detector within the whole spectrum of the visible light, thanks to the application of a spectrometer. The numerical programme elaborated for the analysis of the obtained results has made it possible to present the results in the form of curves showing the relation between the reflectivity of the light and the investigated structure as a function of the angle of the sample position or as a function of the wavelength [5], [6], [7].

3. Determination of the value of the refraction index of phthalocyanine

In some cycles of these investigations samples of thin phthalocyanine layers were subjected to ellipsometric measurements and also to measurements of the surface plasmon resonance (SPR) in order to assess the refraction index of these layers. The idea of the organization of measurements of the investigated phthalocyanine layers involved preliminary ellipsometric measurements, carried out by means of a monochromatic ellipsometer type SE 400. These measurements concerned the quantities of the real part n and imaginary part κ of the complex refraction index of Pc layers for one wavelength and their thickness d. The applied ellipsometer operates using an He-Ne laser, and so the obtained results relate to the wavelength 633 nm. The obtained ellipsometried results (for 633 nm wavelength) were used further for the numerical matching of the spectral theoretical characteristic for the surface plasmon resonance phenomenon to the experimental relation.

The parameters of the layer structure were matched to the angular characteristics of the reflection coefficient making use of the least squares method. In order to find the minimum of the multi-dimensional error function, OPILSKI [8] applied Levenberg–Marquard's method, in which experimental results are matched with the results of theoretical analyses of the layer structure. A measure of matching is the function χ^2. The matching depends non-linearly on the series of parameters a_l. The function χ^2 is a so-called error function determining the deviation of points on the theoretical curve $y(x_i, a_l)$ from the experimental points y_i. The function χ^2 is expressed by the relation:

$$\chi^2(a_i) = \sum_{i=1}^{N} \left[\frac{y_i - y(x_i, a_l)}{\sigma_i} \right]^2$$

where: σ_i – standard deviation of experimental results from their average value, y_i – subsequent values of the points on the experimental curve, $y(x_i, a_l)$ – calculated value of matching with the measuring points.

When the function χ^2 reaches its minimum, the parameters a_l are determined. Basing on those, the unknown optical and geometrical parameters of the layer structure in the function of wavelength can be found. The obtained results of the numerical analysis permitted to determine the dispersive characteristics of the refraction indices of thin phthalocyanine layers.

3.1. Measurements of dispersive characteristics in atmospheric air

Phthalocyanines, being organic semiconductors, are characterized by a complex value of the refraction index [8], [9]. Measurements have made it possible to evaluate the values of the refraction index of phthalocyanine layers, both its real and its imaginary part.

Ellipsometrically measured samples of phthalocyanine layers were deposited on a glass substrate (in the form of thin glass BK7 plate) at room temperature. The temperature of the source of evaporation of Pc amounted to 320°C. Samples of copper phthalocyanines layers, whose refraction index was to be determined, were deposited in pairs on two glass substrates in one single process of evaporation. Each pair contained a sample consisting of a CuPc layer on a glass substrate BK7 and another sample of a CuPc layer deposited on the same glass substrate but with a previously deposited layer of 45 nm gold. The CuPc layers on the glass substrate were measured ellipsometrically, whereas those deposited on the glass substrate with a layer of gold were investigated by means of the SPR-phenomenon. The tested CuPc layer was first subjected to ellipsometric measurements, which yielded the following wavelength values: $\lambda = 633$ nm, $d_{\mathrm{Pc}} = 62$ nm, $n = 1.810 \pm 0.010$ and $\kappa = 0.850 \pm 0.020$.

Then an identical sample of the CuPc layer deposited on glass with a layer of gold was measured by means of the surface plasmon resonance method. The thickness d_{Pc} was assumed to be the same as in the ellipsometric measurements (the thickness of Pc layers is measured by an ellipsometer with an uncertainty of less than 1%). The values of n and κ were determined by matching the theoretical curve to that obtained by measuring the CuPc layer applying the plasmon resonance in the wavelength range of 450–780 nm. The obtained results have been gathered in the form of dispersive characteristics of the quantities n and κ. Figure 2 shows also the dispersive characteristics of copper phthalocyanine with the thickness d_{Pc} equal to 13 nm.

The obtained results indicate that in the case of thin layers the value of the refraction index depends on the thickness of the layer. The obtained characteristics also indicate that the coefficient of extinction κ is higher in the case of the thinner layer, *i.e.*, in the thinner layer the attenuation of light is larger. The value of the real part n of the refraction index, however, increases with the reduction of the thickness of the CuPc layer.

Figure 3 shows the dialogical window of the iterative programme, by means of which the theoretical curve of SPR has been matched to the experimental curve.

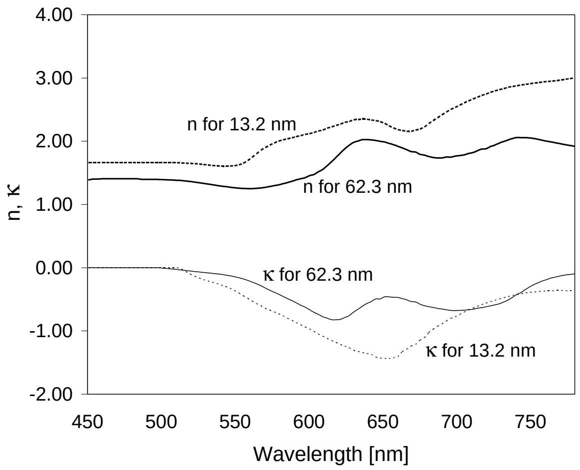

Fig. 2. Dispersive characteristics of the refraction index *n* and the extinction coefficient κ of a CuPc layers, with thickness 13 and 62 nm, in atmospheric air.

The values of *n* and κ of the refraction index of the CuPc layer were adapted to the theoretical model in such a way that the determined values of *n* and κ would correspond to the smallest value of the function χ^2. The diagram in Fig. 3 presents the degree of matching of the curves described above, where each point of the dotted curve corresponds to the measuring point of the coefficient of reflection in the angular

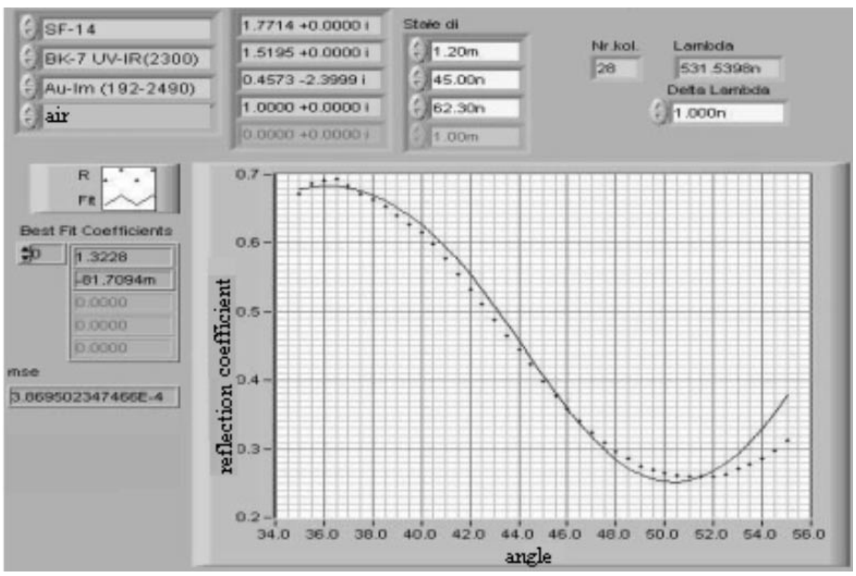

Fig. 3. Matching of the parameters *n* and κ for a wavelength of 531 nm and a thickness of the CuPc layer amounting to 62 nm.

T a b l e. Results of ellipsometrical and SPR measurements of CuPc layers.

CuPc	Ellipsometric results	SPR results
Thickness of the Pc layer	62 .0±0.5 nm	62 nm
Refractive index *n*	1 .825±0 .010	1 .830±0.005
Extinction coefficient κ	0 .845±0 .010	0 .815±0.005

function concerning one exemplary wavelength equal to 532 nm. The full-line curve represents the theoretical curve matched with the experimental one. Moreover, the dialogical window contains also information about the values of optical constants concerning all materials used in the sensing structure (Fig. 1). The dialogue window provides also information about the present values of the thicknesses of the respective layers, determined on the base of an interferometric method or from characteristic of evaporation [3]. As one can see in the dialogue window of the iterative programme presented in Fig. 3, in the case of wavelength λ = 531 nm the values of *n* and κ amount after numerical matching to *n* = 1.322 and κ = 0.817.

The results obtained by adapting to the measurements of the phenomenon SPR differ only slightly from the results obtained for a similar CuPc layer deposited on glass BK7 and determined ellipsometrically. The Table contains the results obtained in the case of both methods of measurements.

We may assume that the resulting differences between the obtained values *n* and κ are due to the fact that the Pc layer, measured elliptically, was deposited immediately on the same glass plate, whereas the Pc layer measured by means of the surface plasmon resonance method was deposited on the gold layer. The different substrates on which the CuPc layer had grown may have caused differences in the structure of the CuPc layer [4]. This finally brought about the differences of the values *n* and κ. Therefore,

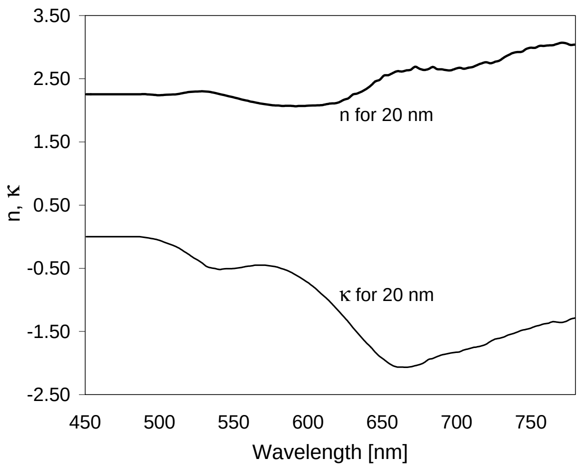

Fig. 4. Dispersive characteristics of the values *n* and κ of the refraction index concerning a lead phthalocyanine (PbPc) layer, 20 nm thick, in atmospheric air.

additional measurements of the CuPc layers deposited on gold layers (of 45 nm thickness), positioned on a glass substrate have been performed. These investigations were carried out making use of the X-ray diffraction method. The results of these investigations together with the results of investigations concerning other phthalocyanine layers were presented in [4].

In Figure 4 one can see the dispersive characteristics of the values of the refraction index, its values n and κ, for a lead phthalocyanine layer with a thickness of 20 nm. In atmospheric air the refraction index n of the PbPc layer varies within the range of 2 and 3, the wavelength ranging from 450 to 780 nm. The coefficient of extinction κ attained its highest values in the wavelength range of 625–725 nm. In the lead phthalocyanine layer the attenuation of the optical wave is more intensive than in a copper phthalocyanie layer, due to the coefficient of extinction (Fig. 4). The highest value of the coefficient of extinction in a PbPc layer of 66 nm thickness amounts to $\kappa = 2.15$.

3.2. Investigations concerning the effect of NO_2 on the refraction index of phthalocyanines

The layer structures of copper and lead phthalocyanine, investigated by means of the surface plasmon resonance method in order to determine the refraction indices, were also tested using this method after having been exposed for 45 minutes to 100 ppm NO_2. The results presented below were obtained by the numerical matching of theoretical relations to experimental ones resulting from measurements of the SPR method, analogically as before.

Figure 5 illustrates the change of the dispersive characteristics of the refraction index affected by the absorption of nitrogen dioxide with a concentration of 100 ppm for 45 minutes by the phthalocyanine layer (13 nm thick). As one can see, the changes

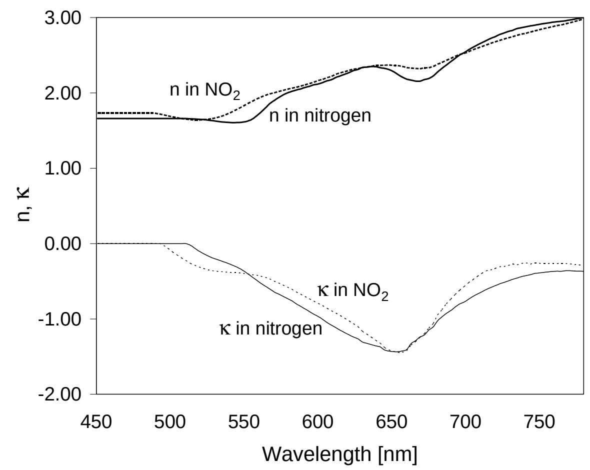

Fig. 5. Changes of the refraction index n and the extinction coefficient κ in a CuPc layer, 13 nm thick, after 45 minutes of exposure to 100 ppm NO_2.

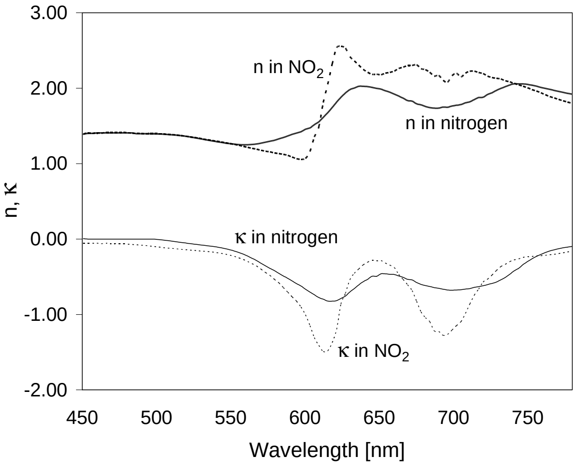

Fig. 6. Changes of the refraction index *n* and the extinction coefficient κ in a CuPc layer, 62 nm thick, after 45 minutes of exposure to 100 ppm NO_2.

of the refraction index *n* and the coefficient of extinction κ affected by NO_2 are rather small in the case of a thin CuPc layer. In the case of a thicker CuPc (62 nm) much more essential changes could be observed (Fig. 6).

In the case of short wavelengths up to about 560 nm no changes of the refraction index *n* have been observed in the CuPc layer (62 nm) affected by NO_2. The value of *n* undergoes, however, considerable changes in the range of 560–610 nm, if exposed to NO_2, where the refraction index *n* decreases its value after the absorption of NO_2 by CuPc, and in the range 610–770 nm, where the refraction index *n* grows after the absorption of NO_2. An interesting characteristic of dispersion of the coefficient of extinction κ has been obtained for a CuPc layer, 62 nm thick. The value of the coefficient of extinction κ reaches its maximum in the case of two wavelengths, viz. λ_1 = 630 nm and λ_2 = 690 nm. At these wavelengths copper phthalocyanine absorbs radiation within the range of visible light [4].

Another dispersive characteristic illustrates changes of the values *n* and κ as a function of the wavelength, concerning lead phthalocyanine with a layer thickness of 20 nm (Fig. 7). At a concentration of 100 ppm NO_2 the refraction index *n* of lead phthalocyanine increases in the entire investigated range of wavelengths.

The value of the coefficient of extinction κ rises under the influence of NO_2 in the range of 450–610 nm, and in the range of 590–780 nm it drops. In both these cases, CuPc phthalocyanine (with a thickness of 62 nm) and PbPc considerable changes of the refraction index *n* and the coefficient of extinction κ were observed, when affected by nitrogen dioxide. Perhaps adequate thicknesses of the investigated phthalocyanine layers might allow to measure the changes of the complex refraction index as a measure of the concentration of nitrogen oxide. This problem requires, however, separate and more detailed investigations.

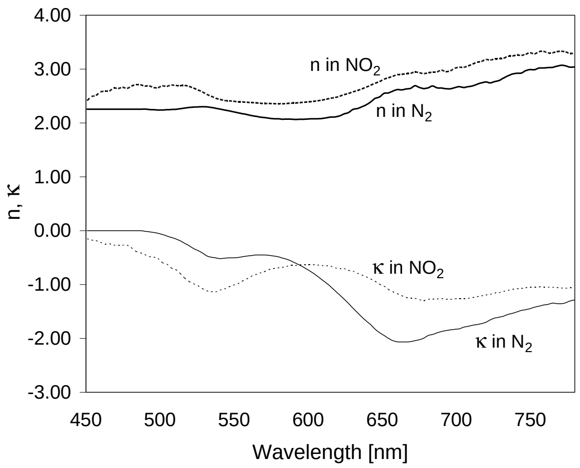

Fig. 7. Changes of the refraction index *n* and the extinction coefficient κ in a PbPc layer, 20 nm thick, after 45 minutes of exposure to 100 ppm NO_2.

Summing up, it ought to be stressed that the crucial problem in determining the dispersive characteristics of the refraction index by means of the surface plasmon resonance method is the exact determination of the layer thickness Pc. Basing on analyses it may be assumed that the uncertainty in the determination of the values of *n* and κ does not exceed 3%.

4. Conclusions

The presented results of investigations indicate the influence of nitrogen dioxide on the values of the optical parameters of thin-layered methalphthalocyanines. The dispersive characteristics of the complex refraction index and its changes due to the effect of nitrogen dioxide on the Pc surface have been determined. In order to determine the value of the complex refraction index the ellipsometric as well as the surface plasmon resonance method were applied. In this way the dispersive characteristics of the refraction index were obtained for copper and lead phthalocyanine in the presence of air and NO_2 with a concentration of 100 ppm in the atmospheric air. All the obtained results display a distinct influence of the exposure of the Pc surface to the effect of NO_2 on the optical properties of thin layeres of the investigated metalphthalocyanines.

The value of the refraction index *n* and coefficient of extinction indicates in the case of thin phthalocyanine layers (bellow 100 nm thick) a dependence on their thickness. In the case of copper phthalocyanine layer of about 60 nm and a lead phthalocyanine layer of about 20 nm the determined dispersive characteristics display considerable changes of the refraction index, both in the actual and in the imaginary part, if affected by nitrogen dioxide with a concentration of 100 ppm.

Investigations of the structure of layers of some selected metal phthalocyanines by means of the X-ray diffraction method have proved that the applied substrate on which phthalocyanine is deposited, such as CuPc and PbPc, influence decisively the structure of the layer [10], [11], and also the values of optical constants (n and κ of the complex refraction index).

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