Spectral studies of nickel-phthalocyanines

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Received June 18, 2019; accepted June 29, 2019; published June 30, 2019

Abstract— The paper presents the results of research of the optical properties of nickel-phthalocyanines (NiPc) in a wide spectrum range of optical radiation. Phthalocyanines belong to the group of organic semiconductors with a complicated molecular structure. Spectral characteristics of their complex refractive index and optical transmission coefficient were determined. Tests were carried out in the range of wavelengths of optical radiation: 300–2500 nm. By means of the Surface Plasmon Resonance (SPR) method, tests were carried out, concerning the possibilities of using nickel phthalocyanines in gaseous sensors of nitrogen dioxide in atmospheres of air and nitrogen.

A continuous increase in the emission of toxic gases to the atmosphere causes increasing interest in gas monitoring equipment [1]. The group of dangerous toxic gases includes, among others, nitrogen oxides NO_2 [2–4]. Photochemical oxidation and production of photochemical smog are the basic and known threats to health and environment, resulting from the emission of nitrogen oxides. The awareness of an immediate health risk posed by nitrogen oxides grows rapidly. It turns out that nitrogen oxides cause irritation of the lungs, bronchitis, pneumonia and a general increase in the susceptibility of the body to viral infections. The amount of nitrogen oxides in the atmosphere increases, on average, by approx. 0.2% annually. Fuel combustion processes, as well as transport and industrial processes, are the main source of air pollution by nitrogen oxides, both within the workplace and atmospheric air. Nitrogen oxides also contribute to the formation of photochemical smog and the greenhouse effect. They have the ability to absorb the Earth's radiation in the infrared range and belong to the so-called greenhouse gases. Their contribution to the greenhouse effect is significant compared to other gases due to the long lifetime of nitrogen oxides in the atmosphere, about 150 years. Nitrogen oxides also contribute to the formation of acid rain.

Considering all these facts, it is necessary to create new precise air condition monitoring systems. The development of gas sensors is heading towards the search for new materials that meet both high sensitivity and selectivity requirements of the gas sensor.

Recently, more and more works have been devoted to the study of electrophysical and sorptive properties of phthalocyanines (Pc) as compounds with a wide range of applications in chemical sensors for analysis of gaseous mixtures [5-11].The aim of the work was to carry out studies on spectral properties of thin layers of nickel phthalocyanine (NiPc). Nickel phthalocyanine was studied in the aspect of its use as an NO_2 detector in the sensor using surface the plasmon resonance (SPR) effect.

Phthalocyanine NiPc as an active material for NO_2 sensors

Phthalocyanines are p-type semiconductors and as such are characterized by acceptor-type conductivity. Adsorption of electron-acceptor gases induces in phthalocyanine generation of charges in shallow acceptor levels. Phthalocyanines have the ability to coordinative bonding the molecules of electron-acceptor gases [2, 4, 9]. NO_2 belongs to the group of electron-acceptor gases. The coordination bond is an indirect bond between the bonds occurring in physical adsorption and chemical adsorption. The coordination bond mainly consists in the fact that the electron doublet comes from one reagent NO_2 and the second reagent (NiPc) supplies only electron gaps (holes). As part of this work, thin layers of nickel phthalocyanine (NiPc) were investigated using spectral ellipsometry as well as reflection and transmission spectrometry. The research was to provide information on the highest spectral sensitivity of the NiPc layer and its thickness, for which the sensor will have a maximum sensitivity to NO_2.

Experimental research on optical properties of NiPc thin layers

Spectral studies of optical parameters of NiPc layers were carried out. Spectral characteristics of the transmission coefficient and the complex refractive index were determined (Figs. 1–2).

Measurements of the refractive index and the transmission coefficient of the NiPc sample were carried out using a spectral ellipsometer, type SENTECH 850. The tests presented below were carried out in the wavelength range 270–2500 nm for nickel phthalocyanine NiPc.

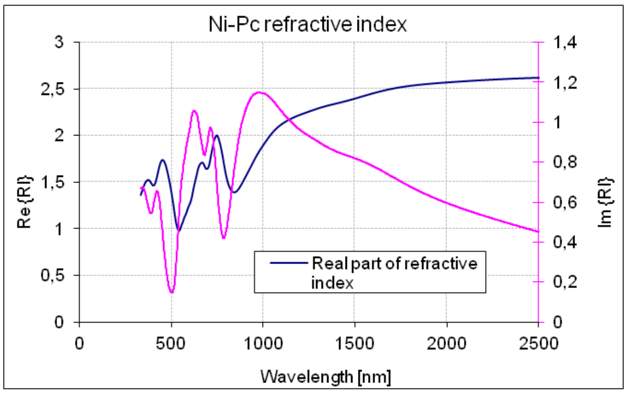

Fig. 1. Characteristics of the refractive index of the NiPc layer (its real and imaginary parts).

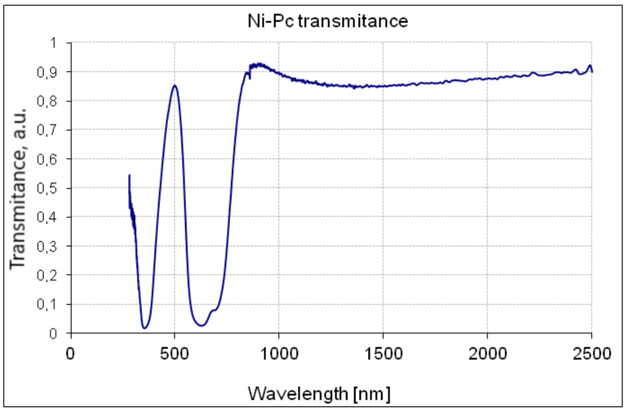

Fig.2. The spectral characteristics of the NiPc transmission coefficient, in the air atmosphere.

Studies on the spectral properties of NiPc layers have shown that optical properties of NiPc are a very complex function of the wavelength of light. Phthalocyanine NiPc has a very strong dispersion of velocity (the real part of the refractive index) but also a strong dispersion of the attenuation factor (imaginary part of the refractive index). The spectral characterization of light transmission is also very complex for the NiPc layer.

Experimental studies of NiPc by the surface plasmon resonance method

The tests of NiPc structures were carried out by the Surface Plasmon Resonance (SPR) method on the stand presented in [2]. The measuring system makes it possible to measure in one measurement series the simultaneous measurement of the signal size as a function of the wavelength as well as that of the position angle of the sample relative to the light source. (The paper presents the results of NiPc spectral tests.) The tested samples were prepared in the form of a two-layer sensor structure composed of a thin layer of gold (about 45 nm) deposited on a glass substrate (BK7 glass) and a thin layer of NiPc phthalocyanine with a variable, controlled thickness.

Plasmon resonance measurements were performed for polarization p (TM) of the electromagnetic wave both in the atmosphere of synthetic air and the atmosphere of nitrogen N_2, as well in the above with 100ppm NO_2. Tests were carried out for four thicknesses of layers of NiPc (10, 20, 30 and 85 nm). Figure 3 shows the spectral characteristics of surface plasmon resonance (SPR) for samples with NiPc layers. The tested structures were obtained in vacuum evaporation processes.

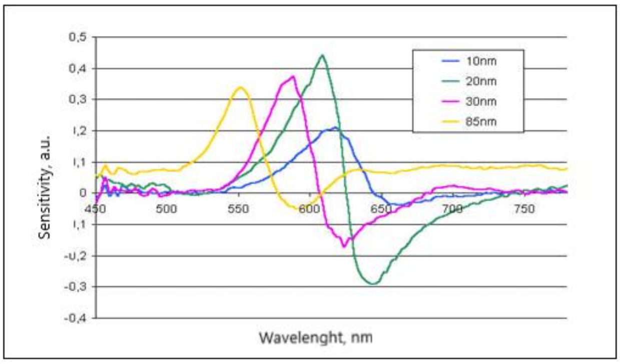

Fig. 3. Spectral sensitivity of nickel phthalocyanine NiPc, for a thickness: 10nm, 20nm, 30nm, 85nm.

Figure 4 shows the sensitivity of NiPc layers of different thicknesses to 100ppm NO_2 measured by the SPR method.

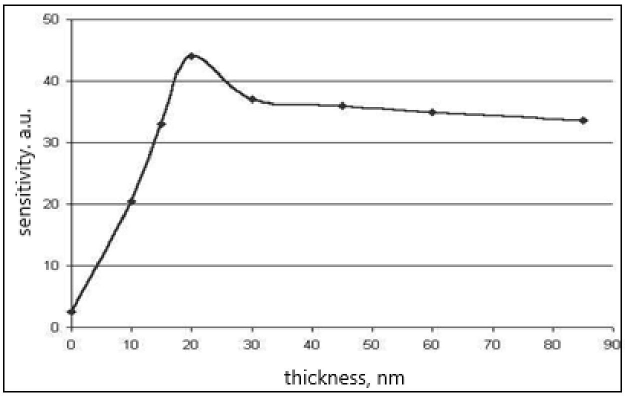

Fig. 4. The sensitivity of nickel phthalocyanine as a function of its thickness [9].

The exposure of the NiPc structure to NO_2 lasted 30 min, and after each exposure cycle the process of regeneration in synthetic air or N_2 took place for 60 min. In Figure 5, the arrows indicate subsequent on/off switching of the NO_2 flow. In the first experiment, the tested nickel phthalocyanine layers were vacuum deposited on a glass substrate at 27°C, previously applied with a 45 nm gold layer. For an NiPc layer thickness of about 20 nm, the deepest plasma minimum was observed, which in this case corresponds to the highest sensitivity of this layer in the group of studied structures. NiPc layers vapor-deposited on a glass substrate at room temperature exhibit sensitivity in a relatively narrow wavelength range of 530–650 nm.

Figure 3 presents the dependence of sensitivity as a function of the wavelength of light for the thickness of the NiPc layer in the range from 10 to 85 nm.

As shown in Fig. 4, in the case of NiPc for a layer thickness above 30 nm, the sensitivity of the sensor structure is high - over 35%, up to the NiPc layer thickness of 85 nm. Therefore, thicker layers can be used in nickel phthalocyanine sensors without losing a relatively high layer sensitivity value (at least about 35% for a 10–85 nm thick range). Further studies of nickel phthalocyanine aimed to check the regenerative properties of the NiPc layer after 100 ppm NO_2 exposure. In these studies, a sensor layer of approximately 30 nm thick NiPc was repeatedly exposed to nitrogen dioxide (dozens of times) at 100 ppm NO_2 in nitrogen.

As results from the research conducted on many layers, the sensor layers of NiPc do not show full regenerative properties after staying for 1 hour in synthetic air (or in nitrogen N_2) with no NO_2 content (Fig. 5).

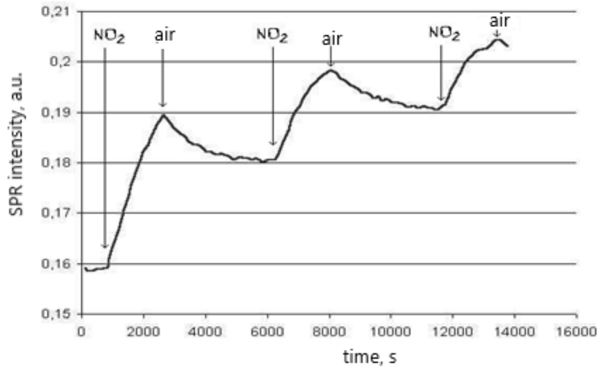

Fig. 5. Changes in light reflectance R from a 40nm NiPc sensor layer subjected to NO_2 exposure cycles at a concentration of 100ppm, alternating with blowing synthetic air.

To explain the effect of the technological process of deposition of NiPc layers on their sensor properties (including regenerative properties) structures were made for which NiPc layers were deposited on glass substrates of different temperature. The research was carried out on structures containing a phthalocyanine layer deposited on a substrate: at room temperature and at a temperature of 170ºC, and at a temperature of –10ºC (Substrate cooling was carried out in a vacuum chamber using a Peltier stack). Of the four tested layers obtained for the temperature of –10ºC substrate, layers with 20 and 30 nm thicknesses were characterized by high sensitivity. This sensitivity was about 25% for 630 nm. Then, the sensor structure with a 30 nm NiPc layer was subjected to detailed tests to determine the degree of regeneration of the layer after previous exposure to NO_2. This sensor layer showed almost 100% regeneration of its optical properties. Also layers of a different thickness applied to a glass substrate at a temperature of -10ºC treated with 100ppm NO_2 showed regeneration of their optical properties in the atmosphere of synthetic air and molecular nitrogen N_2.

In conclusions, nickel phthalocyanine (NiPc) layers showed maximum sensitivity to NO_2in the spectral range of 530 to 650 nm. The NiPc layers tested were 10 to 85 nm thick. The best effect of regeneration of the NiPc layer that earlier absorbed NO_2 was observed for a 30 nm thick layer deposited on a substrate at a temperature of –10°C.

It should be noted, however, that the NiPc sensor layer deposited on a cooled substrate with a temperature of –10°C was characterized by the least mechanical strength among the tested layers.

The conducted researches have shown that nickel phthalocyanine NiPc is characterized by high sensitivity to NO_2 both in air and nitrogen atmosphere.

Spectral tests of the optical properties of nickel phthalocyanine NiPc layers have shown that the optical properties of this material (the coefficient of light transmission and of the complex refractive index) are extremely dependent on the wavelength of optical radiation. When using phthalocyanines in optical gas sensors, the main problem is choosing the wavelength at which the sensor should work.

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