The optoelectronic ammonia gas sensor system based on Pd/CuPc interferometric nanostructures

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Abstract

In the present work the multichannel, optoelectronic ammonia gas sensor system based on interferometric, gasochromic nanostructures has been presented. At the sensing window, on the BK7 glass substrate is immobilized with a chemo-optical, gasochromic and interferometric transducer receptor nanostructure based on Cu-phthalocyanine (CuPc) thin films. The CuPc films were deposited by thermal evaporation. Additionally, to enhance the sensing performance of these CuPc thin films, the surfaces were deposited with ultra-thin film of Pd metal. When a physical-chemical interaction between sensing structure and NH3 gas is taking place on the sensing window of the measuring channel, a interferential color of the sensing element (nanostructure) change and color coordinates of measuring optical signal will change. The color sensor TCS230 detecting the intensity and change of color coordinates RGB of the optical signal resulting from the sensing structure exposure to ammonia gas. Optical ammonia gas sensor displays a very fast response time and a fast regeneration time at low temperature (70°C).

Keywords: optical ammonia gas sensor, copper phthalocyanine thin films, Pd thin film, color sensing, multi-layered nanostructure.

1. Introduction

Continuous development of civilization, forcing the search for cheap and reliable methods for measuring concentrations of various substances: toxic, biological, industrial and other. Extremely important in recent times has become the problems connected with monitoring of concentration of various greenhouse gases, toxic and industrial gases. In recent years, in the literature there have been many reports of the solid state sensors based on various inorganic and organic thin films [1-5]. Currently the most

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popular gas sensing materials are inorganic materials like SnO$_2$ and transverse metal oxides [1-3]. A second important group of gas sensing materials are organic semiconductors (MPc) [5] and conducting polymers (PANi, PPy, etc) [5].

![Image of sensor head](image1)

**Fig. 1.** The schematics of the structure of the 4-channel sensor head, representing the sensor head in optoelectronic measuring gas system (e.g. a two-layer channel configuration).

![Image of sensor system](image2)

**Fig. 2.** The schematics of optoelectronic gas sensor system based on 4-channel configuration of the gas sensing structure. Principle of sensing channel operation.

![AFM images](image3)

**Fig. 3.** AFM images 1 $\mu$m x 1 $\mu$m area comparing the surface morphology of unannealed (a) and annealed (b) ex-situ (220°C/2h @ flow of dry air RH 5.5%) CuPc covered Pd film.

Electrical conductivity and optical properties of metal phthalocyanines (MPc) is known to vary substantially in the presence of oxidizing or reducing gases (e.g. NH$_3$). This occurs due to the change in charge carrier concentration upon adsorption of gas molecules. Therefore, these materials have been extensively studied as chemiresistive gas sensors and optical gas sensors.

In the present paper, we report the preparation and characterisation of an improved ammonia gas sensor with a better sensitivity and selectivity, using a CuPc thin film covered Pd film. Using a very sensitive optical sensing technique, such as white light interference in multi-layered structures and a special configuration of the sensing structure were obtained interested results showing the influence of NH$_3$ gas on the optical (color) sensor response.

2. Experimental

2.1. Technology

At the sensing window, on the BK7 glass substrate is immobilized with a chemo-optical, gasochromic and interferometric transducer receptor nanostructure based on Cu-phthalocyanine thin films, which can interact with a NH$_3$ gas molecules present in the gas mixture. The interferometric structures of a CuPc and
Pd/CuPc thin film gas sensor is shown on Fig. 1. CuPc films were deposited by thermal evaporation in a high vacuum chamber with a base pressure of 2x10^{-6} mbar at substrate temperature 120°C. Additionally, to enhance the sensing performance of these CuPc thin films, the surfaces were deposited with ultra-thin film of palladium metal. This Pd metallic film can act as catalyst that increases the gas dissociation efficiency. A measurement capability of the system is illustrated on the example of the structure equipped with a sensor channels (Fig. 1) with the following configuration: CH1=CH4: 93nm CuPc; CH2=CH3: 93nm CuPc + 5nm Pd.

2.1. Configuration of the sensing channel

In the work the optoelectronic gas sensor system based on interferometric, gasochromic nanostructures has been presented. The color sensor TCS230 detecting the intensity and change of color coordinates RGB of the optical signal resulting from the sensing structure exposure to a specific type of gas (in our case NH₃).

Each optical sensing channel consists of three parts:
- the input port which includes a broadband light source: “warm” white LED,
- multi-layered sensing nanostructure: interferometric and gasochromic,
- the output port which including a silicon color sensor TCS230 detecting RGB signal.

Due to a physical-chemical binding process is taking place on the sensing window of the measuring channel, a interferential color of the sensing element change and color coordinates of measuring optical signal will change as well. By measuring the intensity change of the optical signal RGB, the concentration of a specific gas in the gas mixture will be measured. Configuration and principle of sensing channel operation was showed on Fig. 2.

3. Results and discussion

3.1. Characterization of thin films

The topography of CuPc and Pd/CuPc thin films was investigated and visualized by means of the AFM method. The microstructure changes in CuPc films due to covering Pd films and annealing of Pd/CuPc at different temperatures were studied using AFM. Fig. 3 shows the surface microstructure over a 1 μm x 1 μm area concerning a 93(5) nm thick CuPc covered 5(1) nm Pd film before and after annealing in flow of dry air (RH 5.5%) at 220°C/2h. Thin solid films of CuPc and Pd/CuPc have been studied also using Raman spectroscopy. Fig. 4 shows typical Raman spectra of the Pd/CuPc after annealing in dry air at 220°C.

3.2. The methodology of measurements

The methodology of measurements was based on analysis of the interferential fringe pattern of the layered sensing structures. Each structure of the sensor is made in such a way that it was characterized by interference color. During the interaction specific gas – sensing structure optical parameters of the sensing structure are changed. Due to changes in optical parameters of the structure (refractive indices, absorption coefficient, thickness, etc.) interferential color has changed. Thus the measurement methodology involves registering color coordinates (x, y, z) of interferential color of sensor structure which can be an indicator of specific gas concentration. Finally, each of the four optical channels may have a different architecture of layered sensing structure with different kind of materials.
Methodology was devised for measurement of NH\textsubscript{3} in the concentration range of 3-500ppm in with excellent response and recovery times. Fig. 5. shows typical optical response of the ammonia gas sensor. Measurements were carried out at different relative humidity (from 5% to 70%) of gas mixture, different total gas flows. With this methodology, the optoelectronic sensors showed very good stability in response (at low temperature – 70°C) for a period of few months.

4. Conclusions

A new and original idea of the authors is the specific configuration of the layered sensing structure, sensitive to ammonia, which can be applied in optical and fiber optics gas sensors. An important advantage of the system (sensor head) is the application of optical gas detection, which increases the safety of its use and provides immunity to electromagnetic interference. Another, more important advantage is low operating temperature (70°C) of our sensor. This parameter is important because of less power consumption of the measurement gas system. In comparison to the most commonly used semiconductor MOS gas sensors or catalytic sensor our sensor has reliably worked at significantly lower operating temperature.

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