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NANOSTRUCTURAL SENSOR FILMS OF COPPER PHTHALOCYANINE AND THEIR POLYMER COMPOSITES

A. E. POCHTENNY[1], A. V. MISEVICH[1], I. G. YAMINSKY[2], M. O. GALLYAMOV[2], V. K. SOLONOVICH[3], O. M. STUKALOV[3]

[1]*Belarusian State Technological University*
220050 Minsk, Belarus
[2]*Advanced Technology Center, Lomonosov Moscow State University, Vorobievy Gory*
119899 Moscow, Russia
[3]*Institute of Solid State and Semiconductor Physics, National Academy of Sciences of Belarus, 220072 Minsk, Belarus*

The structure of copper phthalocyanine thin films and copper phthalocyanine - polystyrene composite was investigated by atomic force microscopy (AFM). The results are compared with sensor properties of the investigated films.

1 Introduction

The application of phthalocyanines as gas sensors is based on the adsorption-resistive effect consisting in change of electrical conductivity under selective adsorption of molecules from gas environment [1,2]. Both the molecular properties causing adsorption and the intermolecular interactions ensuring electrical conductivity are important in this case. Phthalocyanine - polymer composites are of interest for investigations of sensing phthalocyanine properties and optimization of the adsorption-resistive characteristics. The formation of a MePc-inert polymer matrix composite allows to change optical, electrophysical and sensor properties of MePc films [3,4].

Scanning probe microscopy is a powerful instrument for investigation of thin organic films. A number of papers is devoted to studies of MePc films [5,6]. In most of them the images of individual molecules were obtained with the help of scanning tunneling microscopy. But the interrelation of structural properties of composite MePc films with sensor properties attracted the least notice in the literature.

The purpose of the present paper is to study the structure of copper phthalocyanine films (CuPc) and CuPc – polystyrene composite with AFM, to follow a temperature effect on their structure, and to compare the structural data with sensor properties of such films.

2 Experiments

We used laser deposition for preparation of composite films [7]. For AFM measurements the films were deposited on substrates of highly oriented pyrolitic graphite and mica. All AFM experiments were performed with scanning probe microscope Nanoscope III (Digital Instruments, USA) in air. We found that the contact mode images, obtained during a single scan, are insignificantly different from the tapping mode images. Repeatable scanning in the contact mode results in smoothing of the film surface. Standard silicon and Si_3N_4 cantilevers were used in all experiments.

In order to investigate the sensor properties, films was deposited on polycore substrates with a counter pins system of nickel electrodes. The sensitivity of the dc conductivity to NO_2 was measured in a dynamic regime at the NO_2 concentration of 2 ppm in dry air at the constant voltage of 10 V in the temperature range from 350 to 430 K.

For investigation of the temperature processing effect upon films structure some samples were annealed in air at 200°C-266°C.

3 AFM investigation

It is known [7] that during sublimation of MePc in high vacuum on substrates kept at room temperature, metastable α–phase is usually obtained. It can be transformed to β–phase by heating or treatment in the solution [8]. Fig. 1 shows a AFM image of CuPc film. The film structure consists of nanocrystallites with ~ 40 – 80 nm in diameter. Optical spectroscopy in the visible range confirmed the presence of α-CuPc. The annealing of CuPc films does not result in noticeable changes of the film structure. There is little increase of the nanocrystallite size.

The structure of the CuPc - polystyrene composite films is similar to that of CuPc film. Nanocrystallites are ~ 100 – 140 nm in diameter. Optical spectroscopy in the visible range shows that the composite film contains CuPc in the form of crystallites of metastable α–phase. The annealing of this films at 200°C brings about the appearance of single needle-like nanocrystallites within ~ 200 nm longitudinal size, ~ 50 nm cross size and ~ 10 – 20 nm of height. Fig. 2 shows AFM image of the CuPc – polystyrene composite film after thermal annealing at 266°C. All nanocrystallites in the film acquired the needle-like shape.

As it is described in [8], the treatment of MePc films by organic solvent can initiate structure reconstruction. Similar reconstruction seems to undergo in CuPc nanocrystallites dispersed in the polystyrene matrix.

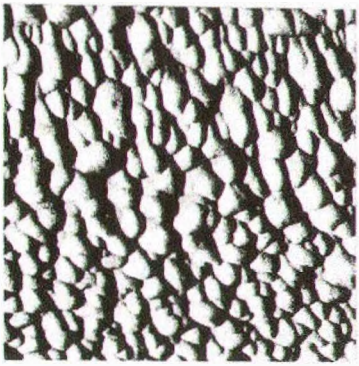

Figure 1. Tapping mode AFM image of CuPc films. Scan size – 985×985 nm^2. Height is encoded by the gray scale (30 nm from black to white).

Figure 2. Contact mode AFM image of CuPs-polysterene composite films. Scan size – 890×890 nm^2. Height is encoded by the gray scale (30 nm from black to white).

4 Gas sensing properties

Measurements of electrical resistance response of the prepared films to NO_2 show that the composite sensitivity is more than that of pure CuPc. A CuPc dispersion in the polystyrene matrix allows to increase the composite response to NO_2 in comparison with the response of pure CuPc films (Fig. 3). Under decrease of CuPc concentration the relative response of composite films to NO_2 increase. The relative response, S, is the ratio of electric current through the film under gas exposure to the current without gas.

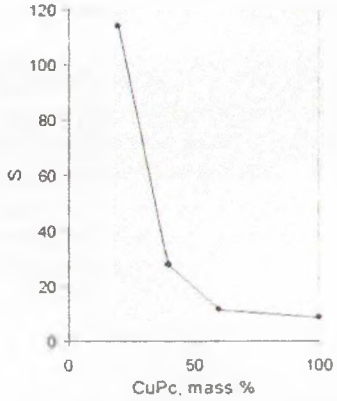

Figure 3. The relative response vs. CuPc concentration in the composite films obtained after 10 min of gas exposure.

The sensor response depends on the gas exposure time, t, according to the Elovich equation:

$$\frac{dS}{dt} = A\exp(-BS),$$

where A and B are the constants.

5 Conclusions

The results obtained indicate that structure of MePc film influences their sensor properties. One possible reason is the changes of access conditions for molecules of adsorbed gas to access MePc molecules dispersed in the polymer matrix. The inert polymer matrix in these organic heterogeneous materials separates aggregates of phthalocyanine and allows to increase their effective adsorption surface. In practice, the dispersion of MePc in polymer matrix allows to improve metrological characteristics of gas sensors. It is a forward-looking method of sensor properties optimization.

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References

1. *Sensors*. Ed. by W. Gopel, J. Hesse, J. N. Zemel. Vol. 2, Part I. (Weinheim: VCH, 1991).
2. J. D. Wright, Progr. Surf. Sci. **31**, 1 (1989).
3. A. E. Pochtenny, D. I. Sagaidak, G. G. Fedoruk, A. V. Misevich, Phys. of Solid State **38**, 1422 (1996).
4. A. E. Pochtenny, D. I. Sagaidak, G. G. Fedoruk, A. V. Misevich, Phys. of Solid State **40**, 712 (1998).
5. J. P. Bourgoin et al., J. Vac. Sci. Technol. B **14**, 5 (1996).
6. F. Rochet et al., Surf. Sci. **319**, 1 (1994).
7. F. W. Karasek, I. C. Decius, J. Amer. Chem. Soc. **74**, 4716 (1952).
8. N. Ueda, Prog. in Organic Coatings **2**, 131 (1973).