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Atomic Force Microscopy of Thin Sensor Films of Copper Phthalocyanine–Polysterene Composite

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The influence of annealing on the structure of thin sensor films of the copper phthalocyanine (CuPc) and polysterene (PS) films obtained by laser sputtering in a vacuum has been studied by AFM. The recrystallization of CuPc as needle-like crystallites has been found at annealing temperatures higher than 200°C. The film annealed at 200°C exhibits the CuPc and PS phases, and that annealed at 250°C contains no polymeric phases most likely due to the evaporation of polymer. The improvement of the sensor properties of the composite films after annealing as compared to those of the films of pure CuPc is explained by their porous structure and a larger effective surface area.

INTRODUCTION

Metallophthalocyanines (MePc) with a high chemical and thermal resistance in combination with the semiconductor properties are referred to as the most promising class of organic electron materials [1]. MePc find application in molecular electronics, solar energetics, and electrophotography [1, 2]. It is especially interesting that these materials are used as highly sensitive and selective chemical sensors [3]. Both the structure of the intrinsic molecule and crystal and supramolecular structure of MePc exert an effect on the parameters of sensors.

The action of the adsorption-resistive chemical sensors is based on a change in the specific conductivity of the film during adsorption of molecules from the environment. Sensors based on films of phthalocyanines of some metals (in particular, copper phthalocyanine) are used for the measurement of the NO_2 concentration in air. The gas-sensitive properties of the adsorption-resistive sensors are characterized by the relative sensor response (RSR), which is the ratio of film conductivities in the presence and absence of the detected gas in the environment. To solve some applied problems, the RSR value of MePc should be increased. For example, ion implantation [4] and temperature treatment which changes the film structure [5] are used for this purpose.

Laser sputtering of the films based on the composite of an inert polymer (in particular, polysterene (PS)) and copper phthalocyanine (CuPc) followed by annealing made it possible to increase RSR of this material as compared with films of pure CuPc. The RSR value depends on the initial weight ratio of CuPc to PS [6]. The best results were demonstrated by the film containing 20 wt.% CuPc in the initial mixture. The preliminary studies by atomic force microscopy (AFM) showed that the annealing strongly changes the morphology of composite films [7].

The purpose of this work is to study the influence of annealing on the structure of composite CuPc–PS films using AFM and to interpret the change in their sensor properties as compared with films of pure CuPc.

EXPERIMENTAL

To obtain composite structures, we used the method of laser sputtering in a vacuum, which allowed us to avoid the destruction of the molecules of sputtered organic substances. The films of pure MePc thus obtained have the polycrystalline structure [1]. The setup for the preparation of thin organic films by laser sputtering was fabricated on the basis of a VUP-5 universal vacuum station. An LGN-703 gas CO_2 laser is the radiation source. It provides a radiation flow density of 30–40 W/cm^2 at a wavelength of 10.6 μm. The laser beam is horizontally introduced into a vacuum chamber through the Ge window, reflects from the metallic mirror, and gets into the crucible with the evaporated substance. The evaporation rate was controlled by a change in the power of radiation introduced into the chamber. The power was monitored by scattering of a portion of the laser radiation on the metallic plate, which was introduced into the radiation field by a micrometer screw. The sputtering rate was monitored by a change in the frequency of a quartz cavity.

The target was an Al crucible filled with a powdered mixture of PS and CuPc containing 20 wt.% CuPc. The sputtering rate was ~0.1 nm/s. To study the temperature influence on the structure, the films were annealed at temperatures of 150, 200, and 250 °C. This range was chosen because the polymorphous transformation of CuPc from the α- to β-form occurs at temperatures of ~200°C [8].

For AFM experiments, films ~10 and 30 nm thick were deposited on mica substrates. The measurements were carried out on a Nanoscope III microscope (Digital Instruments, USA) in the contact mode in air using standard cantilevers.

RESULTS AND DISCUSSION

It was found that multiple scanning of the CuPc–PS composite films first resulted in smoothening of the surface, which increased the average roughness, and then in the partial decomposition of the film. This can be related to the strong effect of the capillary forces on the surface of soft organic films. To decrease the effect of the tip, the scanning rate was

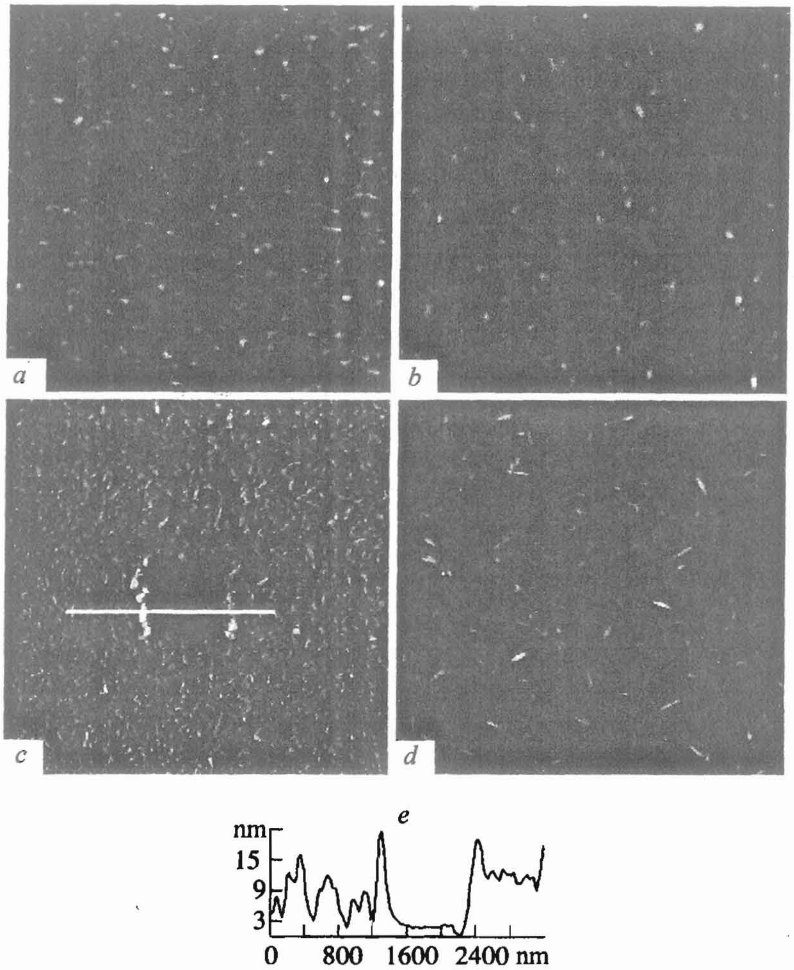

Figure 1. AFM images of the height of the composite films of copper phthalocyanine and polysterene obtained in the contact mode: *a*, before annealing; *b*, *c*, and *d*, after annealing at 150, 200, and 250°C, respectively; frame sizes are 3.5×3.5 μm; *d*, cross section drawn in Fig. 1*c*.

increased and the force applied to the cantilever was decreased. The images obtained by the first scan, which have the smallest distortions, were used for analysis.

During the analysis of AFM images obtained at large scanning fields, we observed inhomogeneous roundish formations ~1 μm in size. These formations were not observed in pure CuPc films [7] and can be due to the evaporation of comparatively large drops of polymer and their deposition on the substrate. The density of these formations was 8–10 per 100 μm^2. The film was sufficiently homogeneous between separate drops.

The AFM images of the CuPc–PS composite film 10 nm thick after annealing in different modes are presented in Fig. 1. No principal change in the morphology is observed on the images of the films non-annealed and annealed at 150°C.

The considerable change in the morphology occurs in the film annealed at 200°C. Nanodimensional extended ("needle-like") aggregates are formed. To control the film thickness, a square hole in the center and the cross section were made by scanning at a high force (Fig. 1*e*). Since the initial film thickness determined by sputtering is of an order of 10 nm, three levels of the height distinguished in Fig. 1 can correspond to the substrate and two components of the composite. The nanoaggregates shifted from the film surface can be interpreted as CuPc nanocrystallites dispersed in the polysterene matrix. Based on the latter, we may assume that at ~200°C, CuPc is recrystallized in the composite in the form of "needles," which can be related to both the polymorphous transformation of CuPc and, first, melting of PS.

An AFM image of the composite film with a thickness of ~30 nm after annealing at 250°C is presented in Fig. 1*d*. The whole film has the "needle-like" structure. The polymeric film is not observed in the image. This can be explained by the complete thermal evaporation of PS, which has the evaporation temperature ~220°C in the crystalline state.

CONCLUSION

The comparison of the results of the AFM studies with the measurements of RSR on NO_2 [9] allows us to conclude the following. Annealing at 150°C does not change the morphology of the composite films. Annealing at 200°C results in the partial recrystallization of the film to form "needle-like" CuPc nanocrystallites, which are shifted from the PS matrix. Annealing at 250°C results in the complete recrystallization of CuPc, and PS is most likely evaporated entirely. This film has a porous structure and a large effective surface area, which results in an increase in RSR of the laser-sputtered and annealed films of the CuPc–PS composite as compared to the CuPc films [7, 9].

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