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SURFACE MORPHOLOGY STUDY OF GAS-SENSITIVE COBALT-CONTAINING POLYACRYLONITRILE NANOCOMPOSITE FILMS

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Abstract. The paper presents the results of studying the surface morphology of cobalt-containing polyacrylonitrile (PAN) films from the standpoint of the theory of self-organization and information theory. It is stated that the films surface is a set of fractals. The correlation dimension D and fractal dimension D_f of the fabricated films were calculated. Using the C++ software package program, mutual information of cobalt-containing PAN films surfaces was calculated, resulting in a correlation between the values of gas sensitivity coefficient and the values of average mutual information of cobalt-containing PAN films.

Keywords: polyacrylonitrile film; self-organization; correlation analysis; fractal analysis; average mutual information.

1. Introduction

Since the middle of the last century, it became known that polymer materials with a system of conjugated bonds exhibit semiconductor properties [1]. It is known that heat-treated PAN is an organic semiconductor, the value of its resistivity is in the range from 10^{10} Ω/cm to several Ω/cm [2], and is used to create various modern electronic devices, including sensors of resistive type [3].

Considering the anthropogenic impact on the environment, it is necessary to use gas sensors with high selective gas sensitivity to obtain accurate information on the quantitative and qualitative composition of the atmospheric air. Therefore, research in the field of creation of gas-sensitive materials with high sensitivity and selectivity is a topical issue in nanoelectronics. In [4] it is found there are self-affinity fractals due to self-organization processes occurring during the formation of organic material at the stage of heat stabilization in metal-containing PAN films that are characterized by high values of gas-sensitivity coefficient.

The surface of the semiconductor films is rough, structure of coatings can be determined by film fabrication technology [5], by deposition conditions and nature of the material. The developed surface-relief structure increases real surface area, which can significantly exceed the topological area. This affects the electrical and other functional properties of the films, in order to evaluate the effect of morphological characteristics, it is necessary to study the connection between surface roughness and fractal dimension.

The difficulty in estimation of the roughness and the size of the surface roughness is in the scale of the measurements, i.e. the scanning step while investigate film surface using scanning probe microscopy [6]. The fractal approach is invariant with respect to the measurement scale [7].

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There are accurate methods of theoretical research of film formation processes and features of their surface. Morphological characterization of surfaces of cobalt-containing PAN films, was explored by the method of atomic force microscopy (AFM). The irregular shape of thin-film surfaces requires such methods for description as the theory of self-organization [8].

To determine the self-organization processes in the cobalt-containing PAN films, the correlation (D) and fractal dimensions (D_f) are calculated. The advantage of the methods of the theory of self-organization is the analysis of the dynamic processes occurring in the structure under the temperature-time regimes of their formation.

However, the method of self-organization does not allow one to assess the degree of ordering of the structure of the polymer material associated with the dynamic processes occurring during its synthesis. The use of information theory allows evaluating relations between morphological characteristics of cobalt-containing PAN nanocomposite films and its sensitive properties. Average mutual information (AMI) value of cobalt-containing PAN films affords to estimate the relation between technological and AFM-image dataset [9]. It allows one to give a correlation model between the values of gas sensitivity coefficient and the value of AMI. Fisher test (F-test) was used to examine adequacy of the obtained numerical model.

The present work aims to identify presence of self-organization processes in the cobalt-containing PAN films, as well as to find relation between the gas sensitivity of the films and the surface morphology.

2. Experimental technique

The gas-sensitive material is a nanocomposite film [10], which consists of PAN and a modifying additive (cobalt concentrations are 0.0 %, 0.25 %, 0.5 %, 0.75 %, 1.0 %). The gas-sensitive material was deposited on a dielectric substrate. To obtain the cobalt-containing PAN films, the incoherent IR-radiation method was used.

To determine the gas-sensitive characteristics, silver contacts formed on the surface of the films. Gas sensitivity of the obtained samples was determined to nitrogen dioxide and chlorine at a temperature of 22 °C. The measured parameter was the resistance of the sample, the value of which changes depending on the concentration of the detected gas in the chamber. The gas sensitivity was evaluated using gas sensitivity coefficient S, which is calculated as

$$S = (R_a - R_g)/R_a, \quad (1)$$

where R_a is the resistance value of the film in air, R_g is the value of the film resistance in the atmosphere of the detected gas (NO_2).

The surface morphology was observed by atomic force microscopy (AFM) using scanning probe microscope Solver P-47. For the investigation of the films, point density of 256 points/1 μm is taken to obtain results, namely a minimum number of points, which are necessary to characterize the fractal behavior of the surfaces [11].

To study the presence of self-organization processes that occur during the thermal stabilization of cobalt-containing PAN films, an analysis of the surface morphology of the samples is made on the base of the AFM image (Fig. 1) and the profile height distribution functions are constructed (Fig. 2).

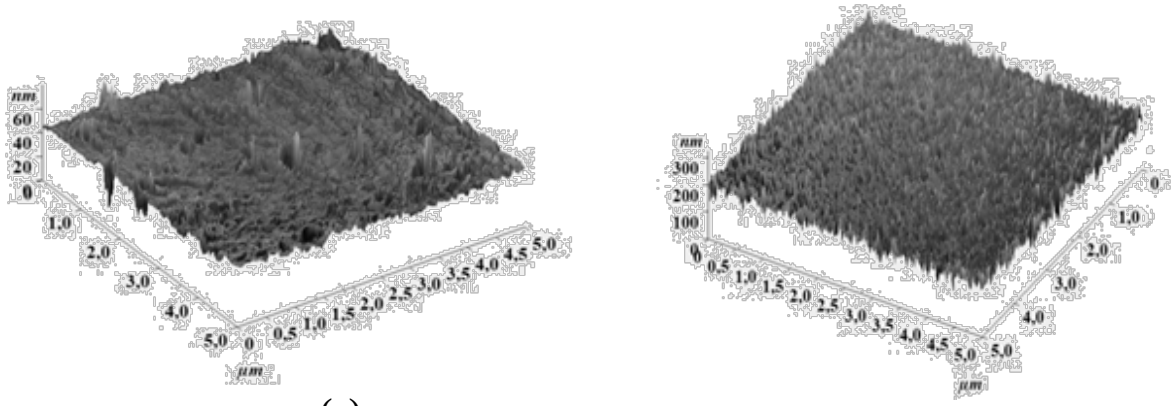
Using the Grassberger-Procaccia algorithm [12], the correlation dimension (D) of the surface of cobalt-containing PAN films was calculated by the Taken method [13]. As a result, not only a numerical equivalent is obtained that corresponds to the dimension identified for a particular sample, but also a frozen picture of the dynamics of the film surface formation is given. Then, in the Gwyddion software package, the fractal dimension of the surface (D_f) was calculated by four methods: cube counting method, triangulation method, variance method,

power spectrum method. The relative accuracy is ± 0.15. Close to the arithmetic mean is the calculation of fractal dimension by triangulation method.

To calculate value of AMI, the algorithm according to [9] was used. Correlation of the AMI values the gas sensitivity coefficient was determined by regression analysis (Fig. 3). For this, correlation coefficient (r) was calculated, then the coefficients of the regression equation were determined by least-squares method. Distributions of AMI value over the surface of cobalt-containing PAN films are obtained (Fig. 4), calculating the AMI in the C++ program.

3. Results and discussion

Figure 1 presents AFM images of samples of cobalt-containing PAN films with different concentrations of the modifying additive.



(a) (b)

Fig. 1. AFM image of the surface of Co-containing PAN films annealed at 450 °C with the concentration of the modifying additive in the film-forming solution: (a) ω = 0%; (b) ω = 0.25%.

Figure 2 shows the convergence of the value of D or the onset of the saturation moment and the presence of a plateau, which indicates the presence of self-organizing structures in the films.

Figure 2,a reveals linear section of the dependence of D on $\log^2(r)$ in the saturation zone (plateau region) that is a sign of deterministic chaos [14] and proves the presence of the self-organization process in the cobalt-containing PAN films. It was experimentally determined the maximum value of the gas sensitivity coefficient of the sample to nitrogen dioxide (S = 0.88 relative units).

The calculation of fractal dimension D_f for most samples showed that D_f values are within $2 < D_f < 3$ and in average equal to 2.2. The latter means that the samples have a small bulk, formed by the planar structures of the thin film. It is possible to assume that the three-dimensionality of the flat structures is attached to loose areas, formed by the cobalt metal oxides embedded in PAN matrix. At the same time, it was revealed that D_f = 3 is characteristic for films with a metal content of 0.25%, which allows us to relate these samples to a three-dimensional space from the position of the self-organization theory.

In order to find the interrelationships in the disordered structure of the surfaces of cobalt-containing PAN films from the position of information theory, the calculation of the AMI of samples surface with different concentrations of the modifying additives was carried out.

Correlation model, based on the calculated AMI and experimental values of gas sensitivity coefficient, was constructed (Fig. 3) and is described by the regression equation:

$$y(x) = -61313.18x + 1.19. \quad (2)$$

The coefficient of correlation between the values of the gas sensitivity coefficient and the AMI of 0.88 indicates a good linear dependence.

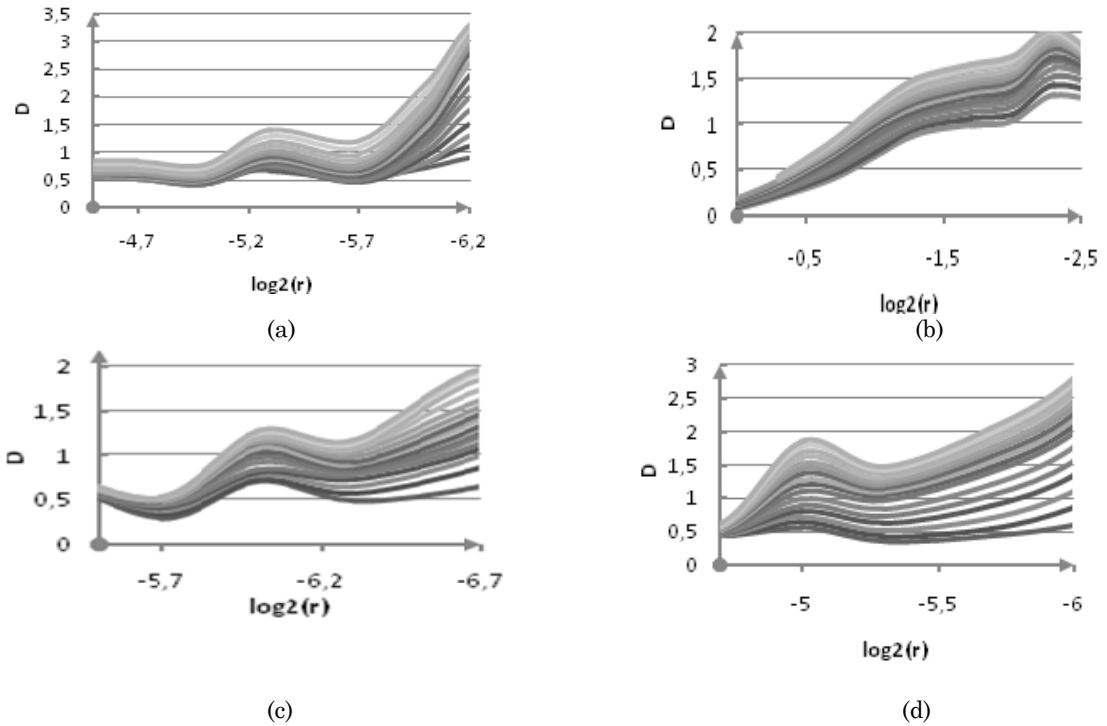


Fig. 2. Dependences of the correlation dimension *D* on the size of the phase space, for the surfaces of the Co-containing PAN films with the concentration of the modifying additive in the film-forming solution: (a) ω = 0.25 %, (b) ω = 0.5 %, (c) ω = 0.75 %, (d) ω = 1.0 %.

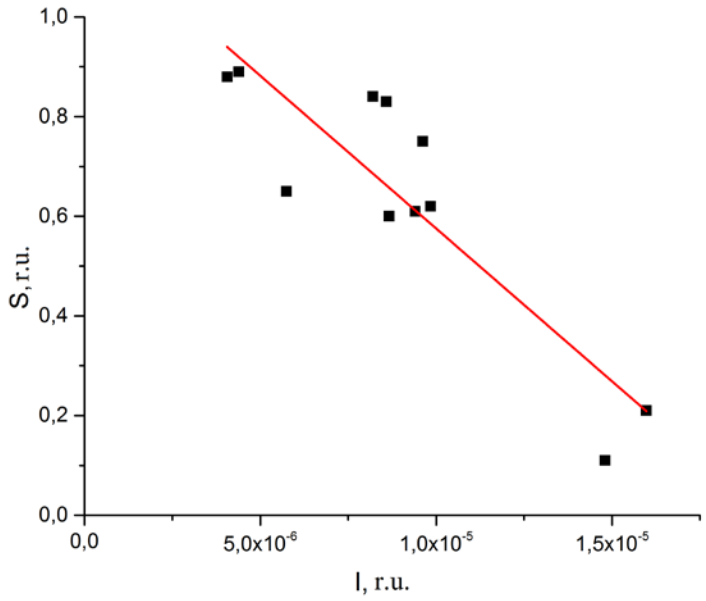


Fig. 3. Correlation of gas sensitivity coefficient and AMI in cobalt-containing PAN films.

Fisher test (F-test) was applied to the gained equation (2): the determination coefficient is $R^2 = 0.78$. In addition, the probability that the obtained model is incorrect corresponds to a value of 0.005. The latter testifies to the significance of this model and the adequacy of the obtained results.

In addition to the foregoing, as a result of calculating the AMI of the film surfaces (I), images of distribution of a given quantity were obtained (Fig. 4).

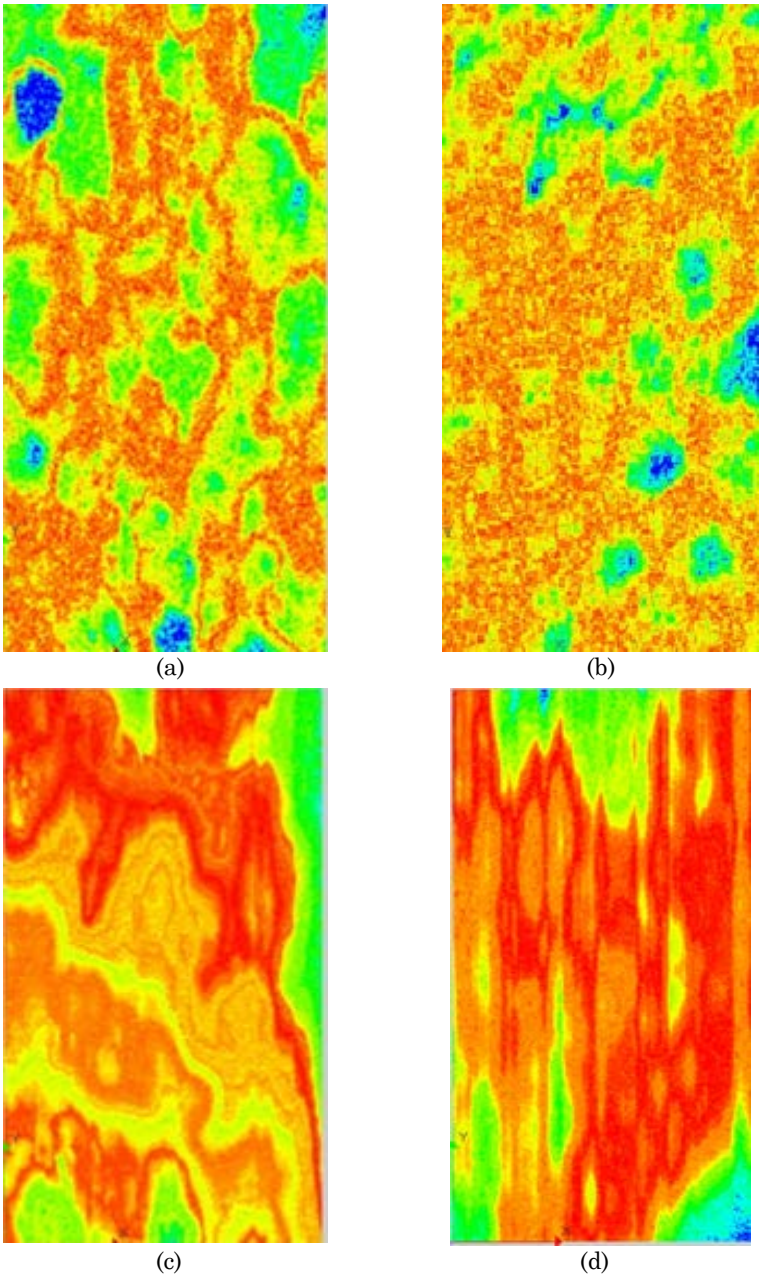


Fig. 4. AMI distribution over the surface of the cobalt-containing PAN films: (a) $I = 1.4 \cdot 10^{-5}$ r.u. and (b) $I = 1.6 \cdot 10^{-5}$ r.u. corresponding to low values of gas sensitivity coefficient to nitrogen dioxide; (c) $I = 0.2 \cdot 10^{-5}$ r.u. and (d) $I = 0.3 \cdot 10^{-5}$ r.u., corresponding to the highest values of gas sensitivity coefficient for nitrogen dioxide.

The results presented in Fig. 4 are consistent with the correlation model shown in Fig. 3. This allows us to conclude that the higher the AMI value, the lower value of the gas sensitivity coefficient to nitrogen dioxide. Fig. 4 indicates that films with similar gas

sensitivity, identical patterns of the distribution of the AMI value are characteristic. Thus, the gas sensitivity of cobalt-containing PAN films can be estimated by AMI distribution without preliminary laboratory analysis.

4. Conclusions

Based on the results of the theoretical study, carried out by the methods of self-organization theory and information theory, it has been confirmed that self-organization processes participate in the formation of cobalt-containing PAN films.

The results of the fractal analysis of the self-affine random surfaces using AFM show cobalt-containing PAN films with a metal content of 0.25%, which are characterized by the greatest values of gas sensitivity to nitrogen dioxide, and are referred to volumetric structures.

Based on the results of the mathematical model obtained, it has been established that there is an inverse correlation between the AMI and the gas sensitivity coefficient values of cobalt-containing PAN films.

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