Self-organization in the thin gas-sensitive Ag-containing polyacrylonitrile films

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Abstract: The surface of thin gas-sensitive Ag-containing polyacrylonitrile films is investigated by a method of atomic force microscopy. The assumption of existence in the studied spatial distributed system of signs of the determined chaos is confirmed with calculation of parameters of nonlinear dynamics. The interrelation between extent of self-organization in films of polyacrylonitrile and their gas-sensitive properties is found.
Keywords: electroconductive organic polymers, gas-sensitive materials, self-organization, theory of information, atomic force microscopy

1. Introduction

Nanocomposite films of metallcontaining polyacrylonitrile (PAN), represent an organic matrix, which structure and properties are changed under the influence of various temperatures, and the particles of a modifying additive dispersed in it, are perspective material for gas sensors [1]. Ag-containing PAN films are fabricated by pyrolysis method under the influence of incoherent IR-radiation from film-forming solutions, undergo transition from a liquid state of substance to the solid-state – this stage is process of self-organization of a material. The structure of the disorder material is formed in nonequilibrium conditions, the substance when hardening changes the properties in time and is distributed non-uniformly in space. Thus a spatial ordered structure is formed in the disorder environment [2]. Methods of nonlinear dynamics and theory of information are applied to the analysis of processes of self-organization in structure of materials: surface structure research of materials with various structural organization and revealing long-range correlations in these structures [3]. It is possible to investigate dynamics of system, measuring any of dynamic variables in one point at regular intervals. Thus the look and dimension of an attractor, number of degrees of freedom, correlation and fractal dimensions of a surface, Lyapunov exponents, average mutual information and other parameters of dynamics are defined. These methods which have been originally developed for the research of systems behavior, changing the condition in time, are adapted for studying of the spatial distributed systems what surfaces of the materials are.

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2. Results and discussion

For carrying out researches a set of samples of Ag-containing PAN films while using different technological regimes was fabricated.

Sensitivity of the films was evaluated using factor of gas-sensitivity S, which is calculated as:

$$S = (R_o - R_g)/R_o,\ R_o > R_g,$$

where R_o – value of resistance of a film in air, Rg – value of resistance of a film in the atmosphere of detected gas.

In view of the material surface is a fractal object, general idea of fractal objects is used for its analysis [4].

The Takens method, well-known in the theory of nonlinear systems, is used to research the dynamics of formation of solid phase of gas-sensitive material of PAN films [2]. Patterns of self-organization processes at the formation of disordered materials, which the PAN films are, can be studied by means of the study of their surface, because their surface is a "snapshot" processes of solidification. Proceeding from this, the fractal dimension D_f of Ag-containing PAN films of the surface profile, obtained with scanning probe microscope Solver P47 Pro (NT-MDT) in tapping mode on the air in the size of areas 5×5 mkm^2 was measured. Step of scanning was determined by the choice of the linear dimensions of the scanning area. Surface scan is carried out with the help a fixed number of points N = 256 × 256 regardless of the scanned area. Distribution function of the altitude profile of the surface $\rho = f(h)$ of studied film, begins on some level of h, taken as zero. Using Image Analysis package we processed 65536 points on the surface image of each sample for constructing this feature. This number of points is sufficient to identify the topology of attractor [2]. As a result of measurement of height profile for the samples, which were carried out along the surface through discrete intervals, get a three-dimensional image of the square surface. In the course of the processing of three-dimensional images of square surface areas by using the Image Analysis program received a graph of the distribution function of the height profile. For data processing Grassberger-Prokaččia algorithm was used [2].

The first Lyapunov exponent λ_r was calculated using Wolf's algorithm [5]. Lyapunov exponents are topological invariants that characterize the spatio-temporal evolution and stability of the system: dynamics of formation of solid-state is determined by the spatial-temporal chaos of a small dimension.

The calculation of the average mutual information I (AMI) was carried out by methods of the theory of information, described in [3]. AMI is the main characteristic of the correlations in nonlinear systems. AMI invariant is relative to the different technologies and allows you to evaluate the impact of different technological factors on the structure of the material.

The studies have shown that application of different temperature and time regimes while forming the polymer nanocomposite films and modifying its transition metal with different percentage concentration lead to significant changes in the morphology of its surface.

Fig. 1 presents the image, obtained by AFM measurements of the surface morphology of a sample of Ag-containing PAN film. The distribution function of height profile *h* (*ρ* is the density of probability) (Fig.2) and the dependence of the correlation dimension $D = f(log_2r)$ (Fig. 3) are given too.

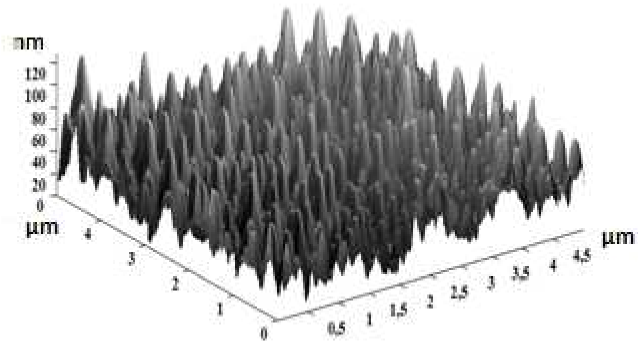

Fig. 1. AFM-image of the surface morphology of Ag-containing PAN film

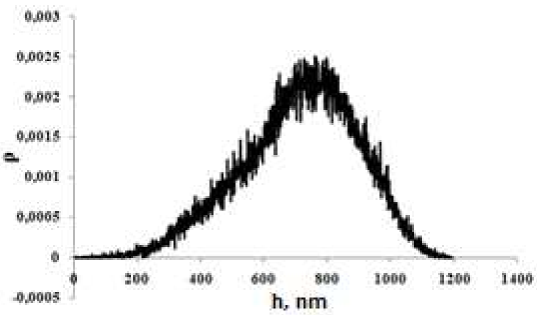

Fig. 2. Distribution function of height profile of Ag-containing PAN film

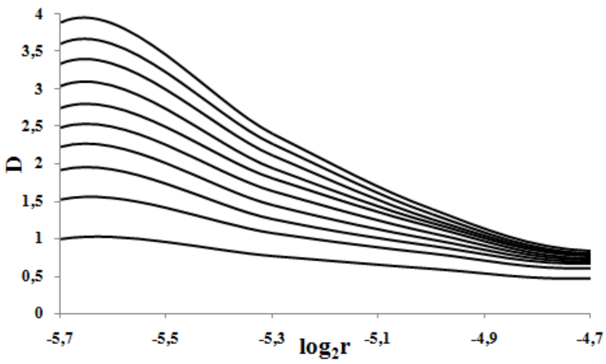

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Fig. 3. Dependence $D = f(log_2r)$ of Ag-containing PAN film

Dependence of correlation dimension $D = f(log_2r)$ allows to testify the presence or absence of self-organizing structures in nanocomposite materials PAN/Ag. The analysis showed the presence of deterministic chaos in the system. It is noted that the surface of the films with the best gas-sensing properties is formed by three levels of self-similar structures.

The studies of the samples revealed that AMI has rather big range in values. AMI increases with the increase of the height of surface profile of films. The samples with the disordered structure represent hundredths of units in AMI values that correspond to theoretical calculations for the amorphous material. Sufficiently high AMI values are observed in the samples with small value of the height of the surface profile (up to 30 nm) and good gas sensitivity (S = 0,46 ÷ 0,53). High AMI values prove presence of long-range correlations in the system, which may be evidence of order as a result of self-organization processes [3].

The dependence of factor of gas-sensitivity on chlorine (107 ppm) and the dependence of AMI value on mass silver content in PAN films fabricated at the same technological regimes, is resulted on fig. 4. Character of the received dependences is similar. The maximal AMI value corresponds the maximal value of factor of gas-sensitivity.

Thus, the calculation of AMI allows to reveal correlations in disordered materials, which conclude a certain interrelation of electrophysical and gas-sensing properties of PAN/Ag films with its morphology of the surface.

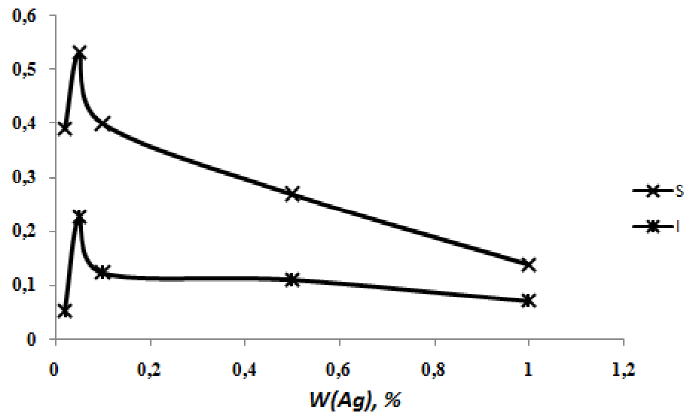

Fig. 4. Dependence of factor of gas-sensitivity (S) and AMI values (I) from silver content by weight in PAN films

For the investigated samples Lyapunov first spatial exponent λ_r which have appeared positive have been calculated. It means, that distribution of substance in space differs from equilibrium. The analysis of Lyapunov exponent testifies, that stability of structure of a material depends on technological parameters of its formation: higher values of temperature of second stage of IR-annealing tend to increase Lyapunov exponent. It is necessary to note absence of correlation

between values of spatial Lyapunov exponent and percentage concentration of the modifying additive in samples.
The results are shown in Table 1.

Table 1. Results of the research the samples of films

The method of film deposition*	The mass content Ag in percent	Sensitivity on Cl_2 (107 ppm)	The correlation dimension	The first Lyapunov exponent	AMI
I	0.1	0.2	1.7	0.0383	0.0898
I	0.02	0.39	1.7 0.9	0.0489	0.0523
C	0.02	0.59	1.6	0.0525	0.1173
I	0.05	0.53	-	-	0.2265
C	0.05	0.63	1.8 1.3 0.7	0.0596	0.0601
I	0.1	0.4	0.8	0.0459	0.1233
I	0.5	0.27	1.4 0.9	0.0415	0.1105
I	1	0.14	0.95 0.65	0.0537	0.0704
C	0.05	0.22	1.1	0.0682	0.1620
C	0.07	0.46	--	--	0.2658

*I – the method of irrigation; C – the centrifugation method

3. Conclusions

The structure of the disorder materials is formed in strongly non-equilibrium conditions with violation of symmetry in the thermodynamically open, non-linear system. These are all the properties inherent in the self-organization. As a result of complex researches the presence of the spatially-ordered structures in the disorder amorphous organic matrix of polymer is confirmed.
During the research it has been established, that greater value of the average mutual information and higher degree of self-organizing answers more ordered structure of the material and the highest values of gas-sensitivity factor.
Thus, on the basis of knowledge of type of dynamics management of nonlinear system of synthesis of a material should be carried out coordinated with internal dynamic processes of substance. It will allow not only to operate effectively the process of growth of the disorder materials, but also to program synthesis of materials for micro - and nanoelectronics with new unique properties.

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