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Nanocomposite films of cobalt-containing polyacrylonitrile as a basis of gas-sensitive material for resistive type sensors

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Abstract. The structure of the metal-carbon nanocomposite based on cobalt-containing polyacrylonitrile (PAN) is studied. The morphology of a surface with the theory of self-organization was analysed. The elemental composition, chemical and electronic states of the elements composing the material films are determined by the X-ray photoelectron spectroscopy (XPS) method. The X-ray diffraction (XRD) method shows that the obtained materials contain crystalline inclusions of CoO, Co_3O_4 and CoO (OH) in the organic matrix of PAN. Gas-sensitive characteristics of the obtained films.

1. Introduction

In advanced electronics we use materials that are nanoscale dispersions of inorganic substances (with particle sizes of approx. 1–100 nm) in the carbon matrix and are metal-carbon nanocomposites. Metal-carbon nanocomposites combine the beneficial properties of organic and inorganic substances, useful from the point of view of practical application. Organic materials are used for design new instruments, including gas sensors and detection of contaminants in the air. Heat treated polyacrylonitrile (PAN) is one of such materials. Is possesses has semiconducting properties, and it is electrical conductivity can be varied from dielectric to metal. To modify the physical and chemical properties of PAN and to obtain its nano-formations, the mechanism of self-organization of the structure as a result of the action of IR-radiation on the polymer was used. PAN is able to adsorb gases efficiently due to the developed morphology of the surface.

2. Methodology

The XPS method was used to determine chemical bonds and compounds in the structure of the organic matrix of cobalt-containing PAN films, the concentration and chemical state of cobalt in the near-surface region of the films. The XPS spectra were registered using a K-Alpha X-ray photoelectron spectrometer by Thermo Fisher Scientific. The source of the X-ray radiation was $K\alpha 12$-line Al ($h\nu = 1486.6$ eV). The vacuum in the analyzer chamber was $2.5 \cdot 10^{-9}$ mbar. The accuracy in determining the binding energy was ±0.2 eV, and that of the element composition was ±0.5 at. %. The XRD was performed using a DRON-6 device. The wavelength of the X-ray radiation of Cu$K\alpha$ was 1.54051 Å.

To study the gas-sensing properties of a material of the received cobalt-containing PAN films measured their resistance on teraommetre E6-13A. Sensitivity of the films estimated by means of factor of gas-sensitivity S, which is calculated as: $S = (R_o - R_g)/R_o$, when $R_o > R_g$, where R_o – value of resistance of a film on air; R_g – value of resistance of a film in the atmosphere of detected gas.

3. Results

Nanoscale films of cobalt-containing PAN were obtained from a film-forming solution under the influence of incoherent infrared radiation at low vacuum ($(5–10)\cdot10^{-2}$ mm Hg) in two stages [1]. The intensity and duration of exposure to IR-radiation allow us to control the properties of the film material by changing the molecular structure of the polymer, which made it possible to obtain thermo-structured PAN films with different electrical conductivity [2–4].

In the process of IR heating a number of chemical transformations occur in PAN and nanocomposites. In composites, the cyclization of nitrile groups and the formation of the C=C and N=N poly-conjugate system occur at low temperatures. Cobalt introduced into the polymer in the form of chloride primarily forms complexes with the –C=N– poly-conjugation system [5–6].

The study of the surface morphology of the film samples of Co-containing PAN was performed using the atomic force microscopy method (AFM) using a Solver P47 Pro (NT-MDT) microscope in a semi-contact mode across areas of 5×5 μm^2 (figure 1). The statistical parameters of the surface morphology were determined using the Image Analysis NT-MDT program. The analysis of morphology of a surface with the theory of self-organization with use of a method of an investment of Takens and algorithm of Grassberger-Procaccia is carried out. It is established that modification of polymer film by cobalt metal materials with different percentage concentration and using of various time-temperature modes of her formation leads to change of morphology of a surface of films. The increase in the percentage content of the modifying additive in the film leads to disappearance of protrusions of the micro-relief, the microstructure acquires a homogeneous character.

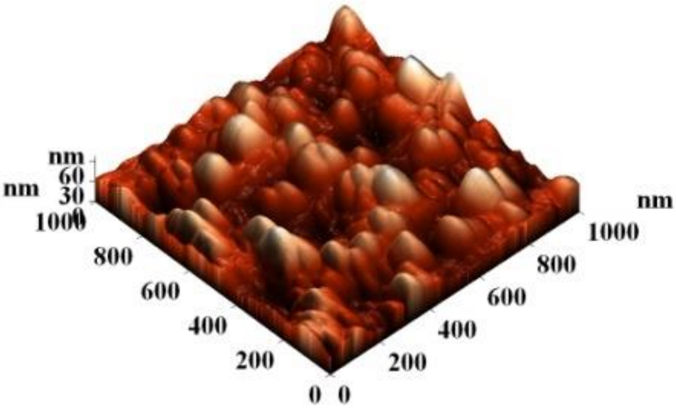


Figure 1. AFM micrograph of Co-containing PAN 0.75 wt. % of cobalt.

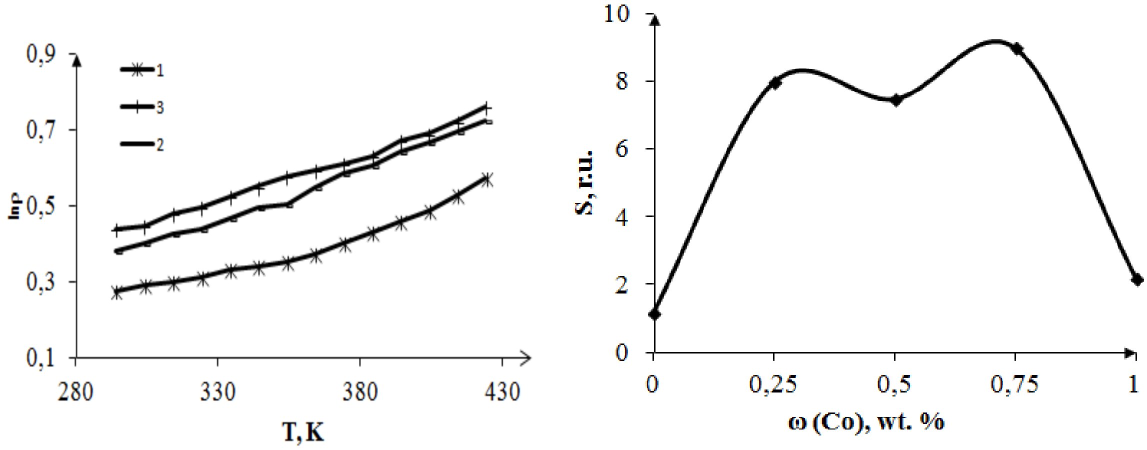
The values of the fractal dimension D_f self-affine surface of Co-containing PAN range from 2.41 to 2.50, so the surface of the investigated films are close to two-dimensionality (D_f = 2), but also have some of the properties of three-dimensionality [7].

The study estimated the effect of temperature of material production film samples and the concentration of modifying component formation to fractal structures and value of the coefficient of the gas sensitive films [8].

The XPS analysis of cobalt-containing PAN films showed that the main peaks related to C 1*s* (~ 285.7 eV), N 1*s* (~ 399 eV), O 1*s* (~ 531 eV) and Co 2*p* (~ 781 eV), can be expanded into several components.

In this study of the films, we took pictures of the spectra of high-resolution of the basic elements of the components that were obtained from the overview spectrum: C, O, N and Co. X-ray phase analysis made it possible to confirm the XPS data on the state of cobalt in the composite film materials. The X-ray phase analysis showed that the samples studied contain crystalline inclusions of CoO, Co_3O_4, and CoO(OH), whose average size was calculated using the Scherrer formula. Thus, the films are nanocomposites in which crystals of cobalt compounds are distributed in an amorphous matrix. The manufactured composite film materials demonstrate semiconducting properties, which is supported by their temperature dependences (figure 2(a)).

The fabricated film materials are generally defined as those having long term properties of metal-containing organic conjugated semiconductor polymer that depend from the IR-pyrolysis temperatures and the weight concentration of the modifying additive in film-forming solutions (figure 2(b)).



(a) **(b)**

Figure 2. The physico-chemical properties of Co-containing PAN: Electrical Conductivity a function of temperature **(a)**: 1 – 0.5 wt. %; 2 – 0.75 wt. %; 3 – 1 wt. %; Gas-sensitivity as a function of metal concentration **(b)**.

4. Conclusion

The structure and morphology of metal–carbon nanocomposite based on PAN with intercalated cobalt have been studied. It is shown that IR-pyrolized PAN films can be applied as a sensitive layer of power-effective gas sensors of resistive type.

The films, whose self-organizing processes are most apparently expressed, show the highest gas-sensitive properties. Processes of self-organizing confirm presence of structures of several correlation dimensions. The parameters of self-organization are dopant concentration and the technological parameters of forming Co-containing PAN material. Studying of influence of technological parameters on properties of materials will allow to operate process of growth of disordered materials effectively, and also to program the synthesis of materials for micro- and nano-electronics with new unique properties.

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