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Surface Activity of Graphite Nanomaterials

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Presents the results of experimental investigation of surface activity of carbon nanostructures: sensor films on the basis of amorphous nanodispersed carbon, carbon nanofibers and disrupted nanographite. The increase in the electrical resistance of such material at a concentration of vapors of acetone in air is 12000 ppm at room temperature in the order of 4 %. It is shown that the growth of the resistance associated with the change in the concentration of conduction electrons in the contacts between the structural elements of the films.

Keywords: Gas sensitivity, Nanodisperse amorphous carbon, Carbon nanofibers, Acetone, The electrical contact of the structural elements.

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1. INTRODUCTION

Research of sorption ability of carbon nanostructures is of great practical and theoretical interest. This is connection to unique properties of nanostructured objects [1-3]. It is known, that their high sorption capacity is related to their following features:

1. High role of the interface, the fraction of surface atoms with decreasing size of the structural element is increased to tens of percent. Properties of boundary surfaces for nanostructured elements is very different from the properties of massives materials and can be controlled.

2. In volume nanostuctured great interface – grain boundaries and triple joints. The total proportion of surfaces of section is

$$K_{\text{р}} = 1 - \left[\frac{L-d}{d}\right]^3, \quad (1)$$

part of grain boundaries

$$K_{\text{г}} = \frac{3d(L-d)^2}{L^3}, \quad (2)$$

and the area ratio of triple junctions

$$K_{\text{Т}} = K_{\text{р}} - K\text{г}, \quad (3)$$

where L – the size of the structural element nanocarbon material, d – the width of the boundary layer.

3. The strong dependence of the electrical resistivity against the square of grain boundaries

$$\rho_{\text{нм}} = \rho_0 + \rho_{\Gamma}\left(\frac{S}{V}\right), \quad (4)$$

where ρ_0 – specific electric resistance bulk material; S – the area of grain boundaries; V – volume [4].

Currently, the most extensively studied sorption properties of nanoobjects such as carbon nanotubes, fullerenes and graphenes, which are closed systems. However, the interest and nanodispersed carbon materials with the structural elements to 100 nm, representing chinoiserie objects with different structure. They are characterized by a large number of the carbon atoms, located on the surface and at the edges with free connection, which makes them more reactive and contribute active adsorption and absorption of gas molecules.

This way, materials based on nanographite are represent of new physical objects, which unique properties to allow their use in various fields of science and technology. The paper presents the results of the investigates the influence of gases on surface activity of nanodispersed graphite materials.

2. EXPERIMENTAL PROCEDURE

For the study of sorption properties of the used films of different nanographite materials:

– nanodisperse amorphous carbon having an average particle size of 50÷80 nm;

– nanofibers 10÷80 nm in diameter and 500-2000 nm in length;

– disrupted nanographite, which is a porous mass, consisting of thin layers 30÷100 nm in thickness, randomly oriented relative to each other.

Initially received a suspension of nano-powders by dissolving in toluene, followed by mechanical dispersion for 30 minutes. The resulting solution in the form of a drop deposited on a substrate made of polyamide with four ohmic gold contacts spaced at 1.9 mm. When dried a solution, on a substrate formed sensor film thickness of 40÷50 μm. Fig. 1 shows images of the structures used nanopowders.

3. RESULTS AND DISCUSSION

Current-voltage characteristics of the sensor films is linear in the electric field for samples of nanodispersed

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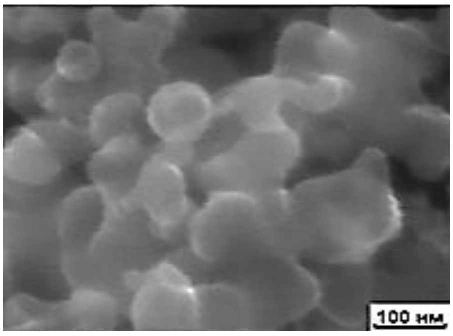
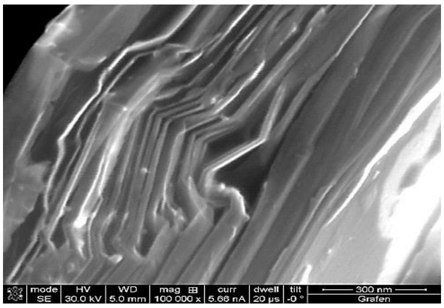
amorphous carbon to $3 \cdot 10^4$ V/m; of nanofibers $2 \cdot 10^4$ V/m; disrupted nanographite to $0,8 \cdot 10^4$ V/m. The magnitude of the resistivity (at $T = 398$ K) were respectively equal to 1,7; 0,37 and 0,048 Om·m.

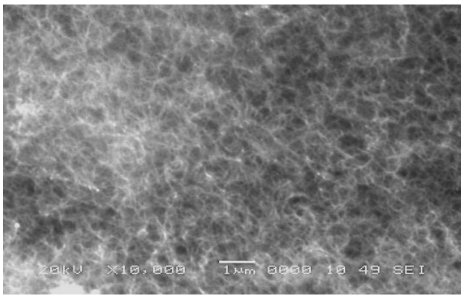
With increasing temperature the resistance of the films decreased, which indicates a semiconducting nature of the conductivity. From analysis of their temperature dependences in the coordinates $\ln\sigma = f\left(T^{-1}\right)$ of the evaluation of the activation energy *W*, the value of which amounted to less than 0,075 eV for the films of disrupted nanographite; 0,13 eV fo films made from nanofibers; 0,11 eV for films of amorphous nanocarbon.



a



b



c

Fig. 1 – The structure of the investigated materials: a – nanodisperse amorphous carbon; b – disrupted nanographite; c – nanofibers

In this paper we investigate the dependence of the sensitivity of the sensor films on the concentration of vapors of acetone (dimethylketone) *C* in the air

$$S_g = \frac{\rho(C)}{\rho_0}, \qquad (5)$$

where $\rho(C)$ – the resistivity with change of concentration of the investigated gas in the air, ρ_0 – initial resistance with $C = 0$ (Fig. 2).

It is shown that for all samples the dependence of the same – with an increase in the concentration of acetone in the air, the electric resistance monotonically increases. On the curves we can distinguish two linear phases: the first in the range of concentrations from 0 ppm to 2000 and second 2000 to 12000 ppm, with a smaller angle of inclination.

Note that the greatest change in resistance is typical for sensor films based on nanodisperse amorphous carbon (Fig. 2, curve 1).

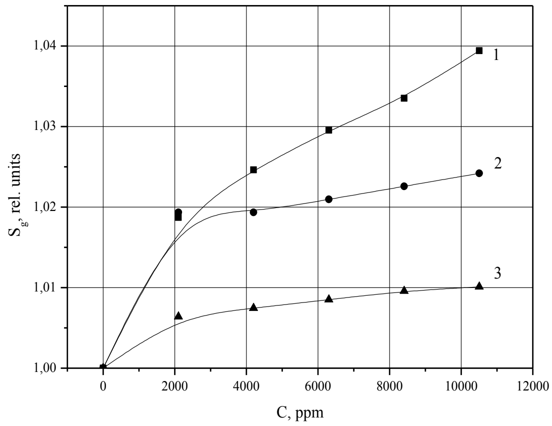


Fig. 2 – The dependence of the sensitivity (relative resistivity) sensor films on the concentration of acetone in the air: 1 – nanodisperse amorphous carbon; 2 – nanofibers; 3 – disrupted nanographite. $T = 298$ K

The value $S_g(12000)$ at $T = 298$ K for this material is 1,04 (increase of the resistivity at 4 %). Also note that currently, the most distribution gas sensors based on polycrystalline metal oxide semiconductor, having a higher sensitivity. For example, in the work [6] investigated samples of thin films on the basis of the composite SnO + (6 %)Y with sensitivity 1,23. However, these patterns are considerably large, compared with the study, the working temperature 550÷750 K.

Properties of electric conductivity of the used sensor films due to the properties of ohmic contacts between structural particles. Whereas that the carbon nanoparticles is characterized by the presence of a large number of dangling bonds, it can be assumed that if contact occurs the restoration of relations of carbon-carbon. The length a bonding in the diamond equal 0,142 nm. The layered structure of graphite, each atom forms strong chemical bonds with other atoms located in the plane at a distance 0,140 nm, while the planes are from each other at a substantially greater distance – 0,335 nm and connected by weak van der Waals bonds. Mechanical properties of the resulting films indicate the presence of granules between the latter type of relations. Therefore, the length of contact between the granules can be taken value $d = 0.34$ nm [8, 9]. It is obvious that in establishing contacts involves random dangling bonds. This implies the presence in the contact area of the high concentration of defects, which determines the number of conduction electrons in the volume. It can be assumed that due to their large reactive, even at room temperature occurs by the chemisorption of molecular oxygen and acetone. This causes a decrease in the concentration of conduction electrons and, as a consequence, the increase of electrical resistance of a sorption film.

In the case of films of nanodispersed amorphous carbon, interdepartmental electrical contacts have the greatest area of the section in accordance with formulas (1), (2) and (3) and as shown in [9] the largest concentration of defects. These factors contribute to relatively high gas sensitivity.

For films based on carbon nanofibers, contacts are made between "thin cylinders", which are located at different angles relative to each other. For nanofibers uncharacteristically large number of dangling bonds, but, as shown in [8] arise between them are van der Waals forces that lead to the formation of point contacts. Obviously, these structures have smaller values K_T, K_p and K_T, accordingly smaller in comparison with films of nanodispersed amorphous carbon gas sensitivity.

Disrupted nanographite is a large number layers of graphene, randomly oriented relative to each other (see Fig. 1c). The value of the structural elements is larger, concentration of defects in the area of contact is much smaller. It explains up to 35 times lower electrical resistivity compared with films of nanodispersed amorphous carbon. As a result, in experiments observed small effect of acetone vapor on the electrical resistance of films of this material.

4. CONCLUSIONS

In conclusion it can be concluded that the sensor films based on nanocarbon structures can be a promising material for gas sensors having *n* operating temperatures compared with the currently used sensors based on metal oxides. Electrophysical parameters of these films and their surface activity are determined by the interrelations of structures of the ohmic contacts.

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