ELECTROPHYSICAL PROPERTIES OF COMPOSITE FILMS BASED ON GRAPHENE NANOPLATELETS COVERED BY METAL NANOPARTICLES

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DC conductivity study showed that thin films based on graphene and graphene containing copper or cobalt nanoparticles, have metallic type of conductivity, but thin films consisting of graphene with magnetite nanoparticles, have semiconductor conductivity. It was found that formation of graphene-Fe_3O_4 film in magnetic field results in the dielectric-metal transition that can be caused by the spin effects in graphene. It was shown that adsorbed oxygen in graphene based thin films acts as scattering centers decreasing mobility of the charge carriers and conductivity as a consequence.

1. Introduction

Pure graphene has unique electrical, thermal and mechanical properties, but it is expensive [1]. Graphene nanoplatelets (GNP) can be obtained by manifold cheap chemical and physical tools, though the properties are worse. Graphene nanoplatelets covered by metal or semiconductor nanoparticles are attractive to improve GNP properties [2,3]. In this talk the results of electrophysical studies of thin films made from pure GNP and GNP covered by Cu, Co and Fe_3O_4 are presented in order to determine the conductivity peculiarities depending on the formulation, external conditions and oxygen adsorbed from surrounding air.

2. Experimental

Graphene nanoplatelets have been obtained by physical tool without any admixtures and chemical defects. Nanoparticles were synthesized and deposited on GNP surface by corresponding reactions made in Institute for Physical and Chemical Problems of Belarusian State University. Nanoparticles of copper and iron oxide have been found to be spherical with diameter of 13.5 and 20 nm, respectively. Cobalt nanoparticles are both spherical (5 nm) and needle like up to 50-100 nm long. Thin films of 100-500 nm were obtained by deposition of water-propanol emulsion on ceramic substrate with the system of nickel electrodes, followed by drying in a drying box at the temperature of 100°C. Graphene-iron oxide films were formed in 0.15 Tl magnetic field (perpendicularly to the film surface) and without it. The morphology and composition of the obtained films has been found with electron microscope LEO-906 (0.1 nm resolution) and LEO-1455VP. The DC conductivity of the films was determined with electrometer B7-57/1 (Belvar, Minsk).

3. Results and discussion

The conductivity temperature dependences were studied by means of cyclic thermo-desorption [4] in 10^{-2} Pa vacuum). The sample is heated up to certain temperature resulting in the decrease of the adsorbed oxygen in the film up to some fixed level. Then the sample is cooling with the same concentration of the adsorbed oxygen, and the conductivity temperature dependence is measured during this process. Then this sample is heated again up to higher temperature, and measurement was repeated at lower concentration of the adsorbed oxygen. As a result, we obtain a set of the conductivity temperature dependences with decreasing adsorbed oxygen in the film in every subsequent heating-cooling cycle.

Graphene nanoplatelets have typical width of 10–20 μm and thickness up to 3 nm. The higher microscope resolution showed that corresponding nanoparticles are physically adsorbed on the graphene surface randomly and enough homogeneously.

Figure1 illustrates the resistance temperature dependences for thin films based on graphene, graphene with copper nanoparticles and graphene with cobalt nanoparticles. The resistance of the graphene films is growing with the temperature increase with a slight super-linearity. Such behavior is typical for semimetals containing admixtures acting as centers of scattering of charge carriers. During the oxygen desorption the resistance of the graphene film decreases that can be caused by decreasing of the concentration of the scattering centers and increasing of the mobility of charge carriers. The curves obtained for thin films made of graphene and graphene with copper or cobalt nanoparticles, are linear in coordinates conductivity-temperature. The presence of copper or cobalt nanoparticles on graphene surface does not affect essentially the character of the temperature dependences of conductivity and resistance, but results in the weaker temperature dependence of electrophysical properties owing to possibly injection of the charge carriers (e.g. electrons) from these nanoparticles.

Figure 2 illustrates temperature dependences of conductivity and resistance or thin films of graphene with iron oxide nanoparticles, formed in magnetic field and without it. These results show that magnetic field applied to the samples during formation process, affect strongly the electrical properties of these films.

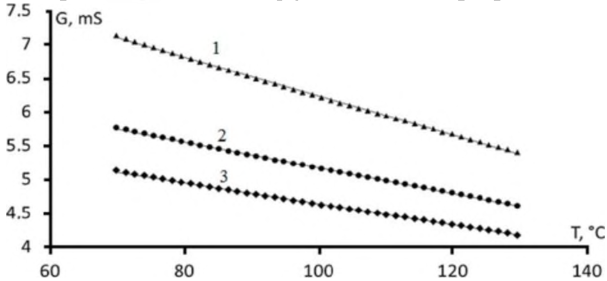

Fig. 1. Temperature dependences of conductivity thin films based on graphene (1), graphene with copper nanoparticles (2), and graphene with iron oxide nanoparticles (3) measured in vacuum under cooling from 130°C.

Graphene – iron oxide films formed without magnetic field has activation character of temperature conductivity dependence with not essential changes of activation energy in the framework of 0.029–0.034 eV. Graphene – iron oxide films formed in magnetic field show temperature conductivity dependences similar to that of graphene and graphene containing Cu or Co nanoparticles. Thus, magnetic field acting during graphene-Fe_3O_4 film formation results in the dielectric-metal transition.

The physical nature of this transition can be explained assuming that conductivity activation energy in graphene-Fe_3O_4 film formed in magnetic field, is the same as in magnetite. It can be simply assumed that formation of graphene-Fe_3O_4 film without magnetic field results in the appearance of continuous conducting cluster consisting from graphene nanoplatelets while in magnetic field the structure consisting of graphene bundles separated by magnetite nanoparticles. However, electron microscopy of both samples shows the same structure though the structure formed in magnetic field is more porous. Thus, this assumption is not enough believable. The more likely explanation of the observed phenomena can be the assumption about partial reorientation of the electron spin in graphene under magnetic field.

In the film obtained without magnetic field electrons have to overcome the potential barrier at the border of graphene-Fe_3O_4, which equals to a half of the width of magnetite forbidden zone, that results in the appearance of activated character of conductivity temperature dependence. Magnetic field acting during film formation results in redistribution of electrons energy in graphene. The part of electrons with spin vector coinciding with magnetic field vector, increases and these electrons have energies near Fermi level. The width of this band is determined not only by thermal energy, but also by energy of magnetic field for

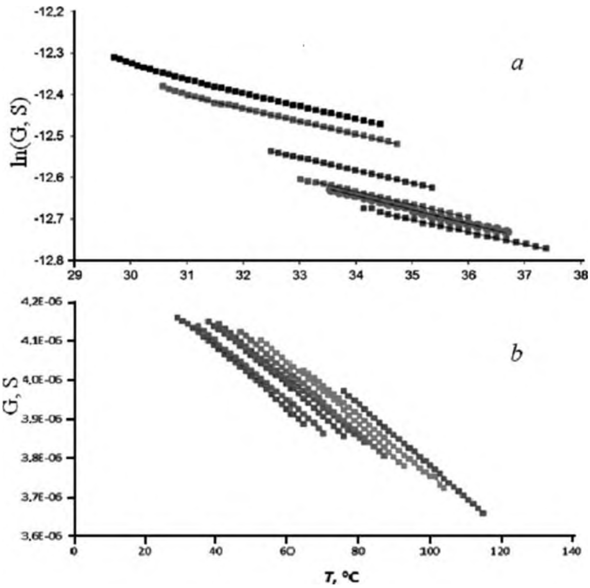

Fig. 2. Temperature dependences of conductivity and resistance of thin films of graphene with iron oxide nanoparticles formed without magnetic field (a) and in magnetic field (b).

reorientation of electron spin. After magnetic field switching off the redistributed state of the electron spin is conserved owing to ferromagnetic nature of Fe_3O_4. As a result, in graphene-Fe_3O_4 film formed in magnetic field redistributed electrons with energy higher magnetite conductivity zone are responsible for non-activation charge transfer.

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