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Temperature Dependence of Resistivity and Current-Voltage Characteristics of the Films of Composites Based on Modified Carbon Multiwalled Nanotubes and Graphite

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A film composites based on modified multiwalled carbon tubes and polymer (95/5 wt. %) Respectively on paper, without the paper by directional spinning from the liquid phase and graphite. The temperature dependence of the resistivity (ρ) in the range T = 77-410 K and the corresponding current-voltage characteristics. Detected irreversible transitions from semiconducting to metallic conductivity in carbon nonotrubkah and a maximum ρ at $T \approx$ 340 K.

Keywords: Current-voltage characteristics, Composites, Carbon multiwalled nanotubes, Graphite.

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1. INTRODUCTION

The unique ability of carbon atoms joined together to form a strong and long chains and cycles have led to a huge number of different compounds of carbon. Carbon multiwalled nanotubes (MCNT) in structure intermediate between graphene and fullerenes, but many properties do not have anything to do with graphene or fullerenes. This can be considered as independent of the nanotube material with unique mechanical, electrical, optical and magnetic properties [1]. Note that many methods of producing nanotubes [2, 3]. The decrease is accompanied by an increase in the diameter of the nanotube energy steric strain, which should prevent the formation of isolated small-diameter nanotubes [4]. Receive different forms of CNTs is achieved by adjusting the special geometry of the cathode of doping elements-catalysts. There is some interest in having thin nanotubes: they can show unexpected physical properties due to the strong hybridization σ- and π-states. One of the amazing facts is the possibility of significant changes in the properties of nanocomposites (such as changing electrical conductivity) with the introduction of the matrix nanoinclusions, which can't be explained on the basis of the classical theory of composite materials. To suggest a possible link the effect of volume fraction of nanoparticles with the formation of transition layers that arise around nanoparticles due to structural changes in the matrix material. Surrounding a nanoparticle modified material increases the effective volume of the particle. Nanoparticles in this case are not only reinforcing additive as stress concentrators, which trigger structural changes in the matrix [5]. Electrical and mechanical properties of the material are determined with a volume fraction and properties of composite inclusions. The volume fraction of the composite nanoinclusions becomes controllable parameter that depends on the thermo-mechanical effects on the process step of manufacturing the composite. To separate single-walled tubes that are net conductors from tubes – semiconductors can pass current at high voltages across the array of tubes with different properties. Tube – conductors with heat and burn, and semiconductors, in which the resistance is higher still. Such an approach is applicable to multi-layer nanotubes, in which the electrons are in contact only with the outer shell. Despite the large number of experimental and theoretical research results, there is currently no clear ideas about the mechanism of the growth of carbon nanotubes are not clearly defined characteristics such as the density of charge carriers, their effective mass, etc. This is primarily due to the weak elaboration of microscopic models of charge transfer. The aim is to study and identify features of the temperature dependence of the resistivity (r)-based composites modified MCNT (MCNT / polymer 95/5 wt. %, respectively) obtained by directional spinning on paper, without paper and carbon / polymer in the range of T = 77 K-410 K and the current-voltage characteristics.

2. PREPARATION OF NANOCOMPOSITES AND EXPERIMENTAL METHOD

For making nanocomposite in PTFE matrix varnish (resin) used MCNT received plasma arc method in the special operating conditions with the average the most common lengths of 100-200 nm and outer diameters of 10-20 nm and the inner diameter of 1.2-3.5 nm. The

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main difference of this method from the usual classical arc plasma technology MCNT growth in the gas phase – the use of a liquid hydrocarbon phase (toluene) at a constant dynamic supply of inert gas argon plasma arc zone, significantly reducing growth temperature MCNT and cheap technical graphite. The advantage of this method – increasing the output of the nanotubes. It turns out the deposit of about 100 g/h at the anode in the conversion of graphite to MCNT to 100 %. Production and modification UMSNT described in [6, 7]. After modifying MCNT injected into the liquid polymer matrix ratio MCNT / polymer 95/5 mas. %, respectively, and stirred for 10 minutes. The resulting stable suspension (suspension MCNT in the polymer solution) was used to form the nanocomposite to the substrate by directional (oriented) spinning of the liquid phase. The polymer is selected so that the melting point more 430 K, the decomposition temperature of 630 K, operating temperature up to 410 K, the specific volumetric electrical resistance 10^9 Om·m, electric strength 11-17 kV/mm. The substrate can be any organic or inorganic materials, such as paper, on which the film thickness MCNT / polymer corresponds to 30 microns. The films were fixed spring contacts on a mica substrate. R The study was carried out in the dynamic mode at a speed of 30-40 K/h temperature range of 77 K-410 K research. Currents and voltages were chosen so that there is no heating of the composite. Composites with outdoor heated furnace in air.

3. EXPERIMENTAL

The results of the study *r* composite films based on nanotubes on paper (Fig. 1). Without paper (Fig. 2). And graphite (Fig. 3) And, accordingly, the current-voltage characteristics, which are linear. At the first heating in the range $T = 77\text{-}300$ K Fig. 1. There is a slight decrease in the smooth ρ.

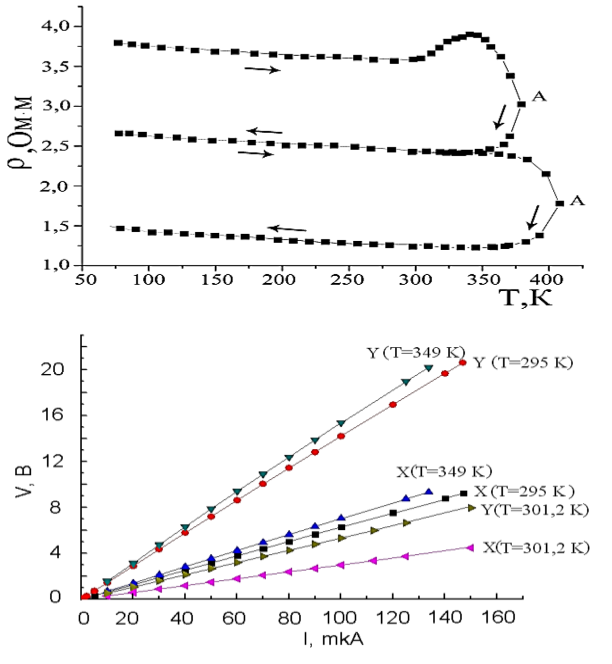

Fig. 1 – The temperature dependence of the ρ of the film thickness of 30 microns based composite MCNT (on paper) and CVC at different temperatures and orientations (x, y)

In this temperature cyclic cooling and heating does not change the value of ρ. At $T > 300$ K ρ increases, reaching a maximum at $T = 340$ K with a subsequent decrease to $T = 410$ K. Cooling from 410 K (A) to 340 K, ρ composite decreases, there is a metallic conductivity and cooling from 340 K to 77 K ρ increases slightly. Further temperature cycling in the range of 77 K-410 K ρ varies in the lower curve (Fig. 1).

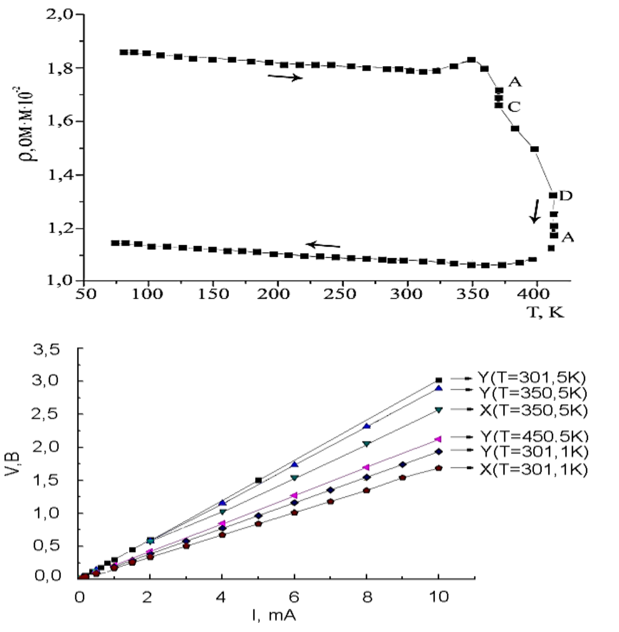

Fig. 2 – The temperature dependence of the ρ of the film based composite MCNT (no paper) and CVC at different temperatures and orientations (x, y)

Annealing of the composite at a constant temperature in the range $T = 300\text{-}340$ K leads to slow growth ρ, and in the range $T = 340\text{-}410$ K decrease *r* with time. The value of ρ decreases at different annealing temperatures (Fig. 2)

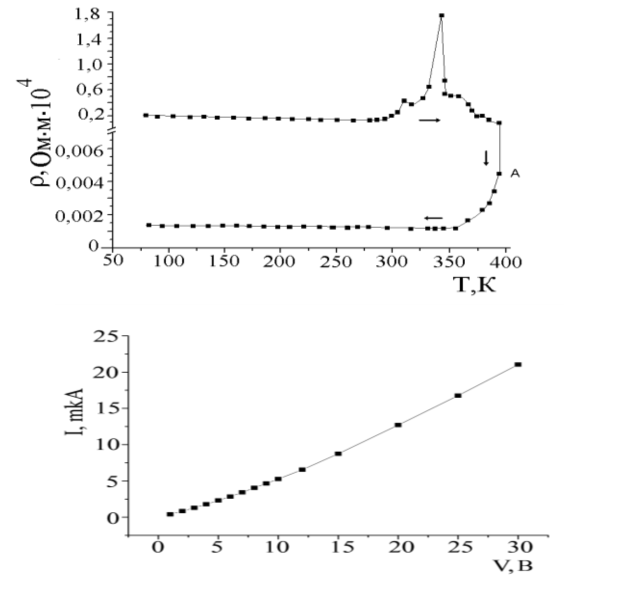

Fig. 3 – The temperature dependence of the ρ of a high-resistance film composite graphite / polymer thickness of 40 microns, and CVC

(DC and DA) for 40 minutes, depending on temperature. In the intermediate temperature range between the increase and decrease ρ annealing there is a temperature at which ρ should not change with time during annealing. These processes are observed for composites on paper and without paper. Note that, like many carbon materials, multi-walled carbon nanotubes are non-ideal structure. They have to be defective, the concentration of which is different and depends on the method of producing nanotubes. Defects directly affect the concentration of charge carriers, and thus the conductivity of the material

Note feature of behavior ρ composite based on graphite (Fig. 3). In the reverse cycle heating - cooling of the film in the range of T = 410 K-77 K ρ varies less than that of the composites based on MCNT. Judging from the temperature dependence of ρ, MCNT fall into two groups. One group r when heating is reduced, which is specific to the semiconductor, the other – r increases, they may be considered as substances with a zero band gap (semimetals) or metals.

The carbon atoms in nanotubes are threefold coordination, and therefore nanotubes - coupled systems, in which three of the four valence electrons of each atom of carbon form sp^2-hybrid orbitals localized and σ- the C-C, and the fourth part in the formation of a delocalized π-system as in graphite. These π-electrons are weakly bound to their atoms, so they probably are involved in the charge transport in the system. In carbon nanotubes there is a relationship between the structure and resistance. In multilayer nanotubes electrons only come into contact with the outer shell. Different shells have different electrical properties due to differences in the electronic structure and charge transfer mechanism in the layers. In semiconducting nanotubes, the band gap is inversely proportional to the diameter of the nanotube. [8-10]. Quantum-chemical prediction was confirmed experimentally [11-14]. Important parameter single-walled carbon nanotubes – chirality, which is determined by the orientation of the graphite plane angle to the axis of the tube. No learned to synthesize nanotubes with desired chiral indices because, if successful, may be able to produce the elements of electronic circuits with any characteristics. Today chirality hardly detectable using the anti-reflection electron microscopy.

As for quasi graphite, the density of state for MCNT near touching the valence band and the conduction band is well approximated by a linear dependence in a wide energy range. This suggests that multi-walled carbon nanotubes will have physical properties similar to the properties of quasi-graphite. Observed maximum ρ at 340 K can be explained as follows. When the environment is cold, the composite material is compressed, creating a lot of gangs of carbon. When heated composite parts are expanding, deforming carbon, reducing the number of gangs, increasing resistance. Simultaneously heating leads to a decrease in the surface density of the nanotubes by the oxidation of the material, the important role played by the iron particles are used as the catalyst. A further reduction of resistance from 340 K to 410 K is accompanied by a transition from semiconducting to metallic conductivity.

4. CONCLUSION

1. The values of ρ does not change under cyclic heating and cooling based composites MCNT and graphite in the temperature range 77 K-300 K.

2. In nanocomposites based MCNT detected irreversible transition from the transition from the semiconducting to metallic conductivity.

3. Found the maximum value of ρat 340 K, which is observed during the first heating of the test materials.

4. Cyclic heating and cooling of relatively low resistance of the composite graphite-based weakly changes ρ to 400 K.

5. Value of r can be controlled by annealing based composites MCNT at temperatures T > 300 K.

REFERENCES

1. S. Iijima, *Nature* **354**, 56 (1991).
2. P.N. Dyachkov, *Carbon nanotubes: structure, properties, and applications. M. binomial* (*Series: Nanotechnology*: 2006).
3. H.W. Zhu, *Science*, **296**, 884 (2002).
4. L.C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, S. Iijima, *Nature* **408**, 50 (2000).
5. R.A. Filippov, A.K. Filippov, A.B. Freidin, *Saint-Petersburg International Workshop on NanoBiotechnologies*, *74* (27-20 November: 2006).
6. A.K. Filippov, M.A. Fedorov, *4-th International Conference on Electromagnetic Processing of Materials – EPM 2003*, *131* (14-17 October: Lion: France: 2003).
7. A.K. Filippov, V.N. Pak, *IWFAS 2007*, *211* (July 2-6: St.-Petersburg: Russian Federation: 2007).
8. R. Saito, M. Fuyita, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rev. B* **46**, 1804 (1992).
9. J.W. Mintmire, D.I. Dunlap, C.T. White, *Phys. Rev. Lett.* **68**, 631 (1992).
10. N. Hamada, S.-I. Sawada, *Phys. Rev. Lett.* **68**, 1579 (1992).
11. P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, *Sciense* **278**, 100 (1997).
12. T.W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi, T. Thio, *Nature* **382**, 30 (1996).
13. C.L. Kane, E.J. Mele, J.E. Fischer, R. Lee, P. Petit, H. Dai, A. Thess, *Europhys. Lett.* 41, 683 (1998).
14. T. Pichler, M. Knupfer, M. Golden, *Phys. Rev. Lett.* **80**, 4729 (1998).