Features of electromechanical properties of carbon nanostructures

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Abstract: *Non-standart properties of carbon nanomaterials and nanostructures open wide possibilities of their application. The electrical resistance of bulk arrays of carbon nanotubes in cyclic loading-unloading processes was studied. It is shown that when the volume of the powder sample decreases, the resistance first decreases sharply, and at a certain degree of compression the process of its change begins to occur more smoothly, which is associated with increased contacts between neighboring nanostructures and van der Waals bond between them.*

KEY WORDS: *CARBON NANOTUBES, NANOMATERIALS, ELECROMECHANICAL PROPERTIES, RESISTANCE*

Introduction

The study of carbon nanotubes properties is due to their unusual properties: they combine high strength and elasticity, thermal and electrical conductivity. Mechanical deformation and defects affect the electronic structure, concentration of charge carriers, electrical, emission and other properties. Defects occur both in the process of synthesis (growth and gas impurities) of CNTs, and under external influences, especially during radiation exposure.

The geometry of CNTs changes under the action of elastic deformation, which can significantly deform the profile of the entire nanotube, or locally at the intersection of contact nanotubes, which affects the electronic structure at the point of deformation, which controls the electrical properties of not only one nanotube but the entire CNT array. The electrophysical properties of isolated CNTs are being studied in many laboratories around the world for their use in nanoelectronics. The properties of an individual nanotube are to some extent known – along the axis it is a good conductor of current and heat, but in the radial direction the movement of charge carriers and phonons is limited by the outer cylindrical carbon layer. To expand the scope of CNT, it is necessary to increase the flow of heat and current, for which it is necessary to investigate their properties in bulk or consolidated state. In bulk CNTs usually do not conduct electricity, but with little compression the situation changes.

In this work is shown that the restrictions for current carriers are removed during the deformation of the CNT array by compression, as a result of which such an array passes into an electrically conductive state. It should be noted that multilayer CNTs have a very low concentration of charge carriers, which limits the scope of their possible application, but the mobility of charge carriers is three orders of magnitude higher than in copper. Therefore, it is important to find ways to increase the concentration of charge carriers and electrical conductivity in the CNT array and increase the flow of heat and current. The influence of CNT orientation, degree of packing (ordering) of CNTs in the array, number of contacts, their total area, nature of connection between CNTs, type and number of defects in CNTs on electrical and thermoelectric properties was also investigated. In this regard, the CNT array can have a wide range of properties, which opens up perspectives for further research and expansion of applications.

Experiment

The electrical resistance of the CNT array was measured on a fairly accurate installation, which allowed to record voltage up to 10^{-5} mV [1]. Resistance was measured using a dielectric cylinder, the bottom and piston of which served as electrodes. The density of the material was changed by means of a movable piston. After reaching the maximum compression, the piston was gradually lifted and at the same time the electrical conductivity of the elastically relaxing material was measured. Due to the elastic relaxation, the electrical contact of the test material with the electrodes was maintained, which allowed to measure the electrical conductivity during unloading. The cessation of the relaxation expansion of the material led to the breaking of the electric circuit and a sharp increase in the electrical resistance between the electrodes (relaxation transition).

Thus, the inverse measurement is that when reaching the maximum density during the direct measurement, the material elastically relaxed and, starting from this value, went in the opposite direction of decreasing density, i.e. gradually raised the micrometer rod, as long as the test material retained electrical contact with electrodes.

Results

The electronic properties of carbon nanotubes are determined by their unique anisotropic structure and high electronic conductivity. A distinction should be made between the electrical resistivity of individual nanotubes (single-layer and multilayer) and the resistivity of a material or composite consisting of such tubes. The resistivity values of individual nanotubes, which are measured by different groups, can differ from each other within several orders of magnitude. This is due to differences in the structures of nanotubes, chirality, the presence of defects in the hexagonal layer, attached radicals (-OH, -CO, etc.), which change the position of the valence band and the conduction band.

Multiwall carbon nanotubes (MCNTs) differ from single-layer ones by a wider variety of shapes and configurations. Most often, these are coaxially nested single-layer nanotubes. The situation for an array of individual nanotubes or a material consisting of them may be different due to the presence of contacts between adjacent nanotubes, electrodes, contact pressure and other factors. When the volume in which the array of electrically conductive CNTs is placed at a certain critical value, the nanotubes can be closed with the manifestation of characteristic signs of percolation transition. The latter is known to be a geometric analogue of the metal-insulator transition [2].

The electrical conductivity of a material consisting of nanotubes largely depends on the degree of contact between adjacent nanotubes, as well as on the presence and composition of impurities. Due to its physicochemical properties and significant potential for applied use, CNTs are the subject of research in many laboratories around the world.

The electrical characteristics of the CNT bulk array obtained by the gas phase deposition method on catalysts Al_2O_3-Fe_2O_3-MoO_3 were studied. TEM- image is presented in fig. 1. In accordance with the basic assumption of transmission microscopy that the intensity of the image contrast directly depends on the amount of scattered matter, it follows that the darker areas in the positive images correspond to denser areas of the sample or heavier atoms present in the sample, narrow dark bands that observed, attributed to the walls of nanotubes. This indicates an extremely high elasticity of the array of undirected CNTs.

The statistical distribution of nanotubes by outer diameter showed that the diameter of nanotubes is in the range of 10-20 nm. When the volume in which the interacting nanotubes are placed decreases, the electrical circuit closes and the system (nanotube-air) goes into a conductive state. (fig. 2)

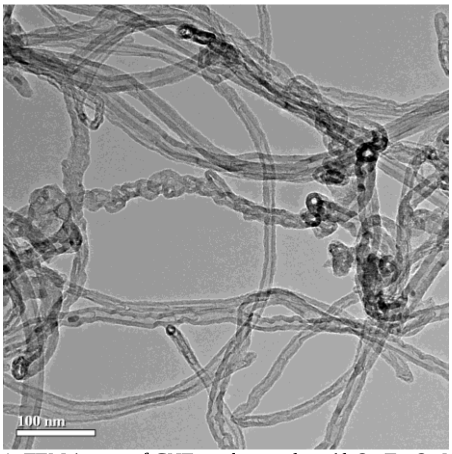

Fig. 1. *TEM-image of CNT on the catalyst Al_2O_3-Fe_2O_3-MoO_3*

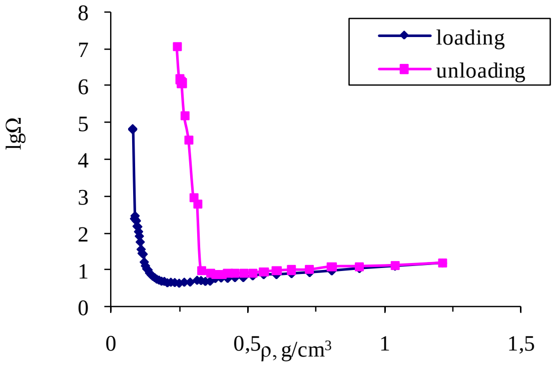

Fig. 2. *Dependence of the logarithm of the electrical resistivity Ω of an array of multilayer carbon nanotubes on the change in its density ρ during compression and subsequent unloading*

When compressed under the piston, the resistivity drops abruptly by 4 orders of magnitude, reaches a minimum value of 4,37 (Ohmcm), at a density of 0,25 g/cm^3. Subsequent compression to a density of 1,2 g/cm^3 leads to a slight increase in resistivity to 15 (Ohmcm). Deformation leads to the appearance of mechanical stresses, which contribute to the emergence of additional potentials at which the conduction electrons are dissipated during the passage of current. This causes an increase in electrical resistance.

The observed effects (Fig. 2) are explained by the action of two competing mechanisms: 1) an increase in the total area of contacts between neighboring CNTs, which contributes to the growth of electrical conductivity; 2) elastic deformation, which contributes to the reduction of electrical conductivity.

After compressing the sample to $\rho \approx 1.2$ g/cm^3, the piston was lifted and at the same time the electrical resistivity of the elastically relaxing material was measured, which is restored to the maximum value and provides contact with the electrodes. The reverse course of the curve $\Omega(\rho)$ in the process of elastic relaxation of the CNT repeats the course of the curve when compressed over a large section of the piston path. Completion of the relaxation process was recorded by a sharp increase in electrical resistivity $\Omega(\rho)$ and breaking of the electric circuit. This process was fixed by the density of the relaxation transition. The appearance of hysteresis between the transition to the conductive state and the relaxation transition is caused by inelastic processes associated with the displacement of nanotubes during deformation.

The array of carbon nanotubes was subjected to loading-unloading processes cyclically.

After four cycles of load-unloading deformation of the CNT array, the density of the transition to the conductive state increases from 0.08 to 0.22 g/cm^3 (Fig. 3), which almost coincides with the relaxation transition ρ_{rel}=0.23 g/cm^3, and the curve $\Omega(\rho)$ practically repeats a course of a curve of loading-unloading for the subsequent cycles. This indicates the ordering of CNTs in the process of cyclic deformation.

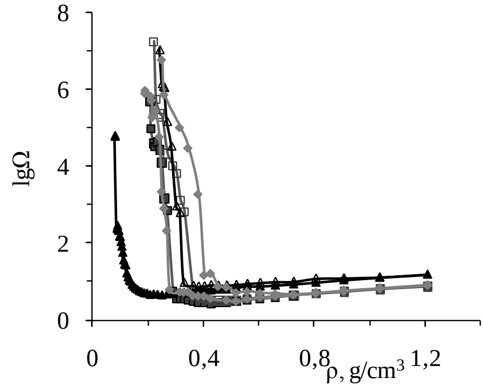

Fig. 3. *Influence of cyclic deformations on the electrical resistance Ω (ρ) of multilayer CNTs: for 1, 2 and 4 measurement cycles: 1 - ♦, 2 - ♦, 4 - ■ – loading, 1 - Δ, 2 - ●, 4 - □ – unloading*

The thermo-EMF method provides important information about the state of the electronic subsystem of the nanocomposite with nanotubes. In [3] it was found that the highest value of thermo-EMF is observed for the most purified CNTs and is α=23,7 μV/K, and the calculated electron concentration at 0 K is n_e=1,3 10^{19} cm^{-3}. Less purified nanotubes, ie more defective, have a smaller value of α and a larger n_e, so an increase in the concentration of electrons reduces the coefficient of thermo-EMF, which has a plus sign.

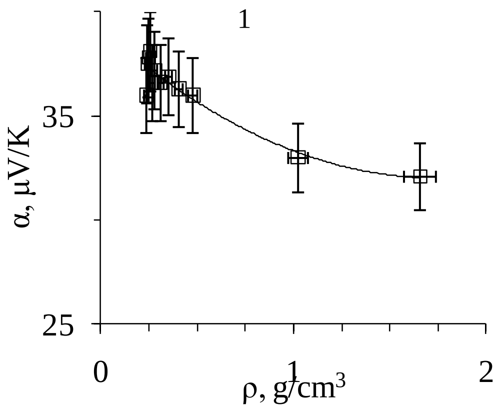

Fig. 4. *Dependence of the Seebeck coefficient (α) on the density (ρ) of the CNT array obtained on the catalyst Al_2O_3-Fe_2O_3-MoO_3*

Deformation of the CNT array leads to a slight decrease in the Seebeck coefficient, which may be due to the suppression of the effect of phonon hole capture when the CNT is reoriented to a predominantly perpendicular direction of phonon flux. The maximum value of α for CNTs is 36 μV/K (Fig. 4) at array densities of 0,2-0,5 g/cm^3, and with increasing density, the coefficient α gradually decreases and reaches values of 32 μV/K at ρ=1,7 g/cm^3.

Conclusions

In the process of cyclic deformation of the CNT array, there is an increase in electrical resistance by 4-5 times at a density ρ = 0,86 g/cm^3, which indicates the ordering of nanotubes and the appearance of the predominant orientation of the axis perpendicular to the current lines.

The Seebeck coefficient of the CNT array significantly depends on its density, orientation, the presence of defects and is in the range of α = + (26-34) μV/K. A positive sign indicates a predominantly hole contribution to the electrical conductivity in the radial direction.

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