Synthesis of conductive films based on oxidized carbon nanotubes

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Abstract. This talk presents the work related to creation of films based on carbon nanotubes (CNT). CNT films have a great significance in chemistry world because of possibility of obtaining very strong, conductive and flexible films based on special CNT properties. These films also can be very useful in optical applications, for example, as sensing element of IR and THz optical sensors. But achievement of a cheap and strong film still remains a difficult task because of inert CNT structure. In this paper singlewalled and multiwalled carbon nanotubes were used. The film was formed by using oxidation, filtration and annealing processes. This technology can be the cheapest because of small quantity of chemicals and needs to be investigated. The film demonstrates high temperature resistivity without deformation.

1. Introduction

Carbon nanotubes were discovered in 1991 by Iijima [1]. This material has received rapid distribution and now has increasing relevance. This is due to the fact that carbon nanotubes have excellent properties such as high conductivity, high thermal stability, high surface-to-volume ratio, and can be used in various applications, such as conductive polymer material, sensor sensing element, high-strength material, etc..

A few main directions in the development of techniques related to CNT for now are the alignment of carbon nanotubes and their functionalization, for example, for the task of creating gas sensors [2]. Also a current task is to create a variety of coatings and films of CNTs. At the moment, the creation of various films is not only a chemical task (fabrication of durable polymers [3]), but also physical, in particular, in the field of optics due to the need of development a coating with the highest absorption coefficient of radiation, sensors of different ranges (in particular, IR [4] or THz ranges [5]).

Fabrication of CNT films can be carried out in two ways. The first method – physical - is the formation of the required structure in the process of direct synthesis of CNTs [6]. The second method – chemical - is carried out by forming strong intermolecular bonds between individual nanotubes that causes a change in their physical and chemical properties [3]. This method is more preferable because of its simplicity and allows you to change the chemical properties of ready-made films, which gives more opportunities for their use for a wider range of tasks.

However, the technology of creating such films has a number of disadvantages that must be eliminated. These disadvantages are: the complexity of precise control of film thickness, limited choice of chemical treatment for creation of intermolecular bonds between CNTs, the need of using...
additional physical methods, such as ultrasonic treatment or UV radiation, to adjust the flow of the desired chemical reaction. Also, problems may be the selection of solvent, the complexity of manipulating nanotubes, etc.. Chemical creation of the film, usually, requires strict observance of all reaction conditions – temperature, time, correct composition of chemicals. Moreover, these conditions must be carefully chosen to achieve the desired result.

When chemical treatment (for most cases functionalization is added) is applied to such a new material as carbon nanotube, it is necessary to take into account that not all methods allow to obtain the desired result, since the physical and chemical properties of CNTs strongly depend on the properties of the crystal lattice of CNT, such as: the length of the nanotube, its diameter, chirality, the percentage of impurities, defects in the crystal lattice of CNT, the number of layers, etc. [7]. Already have been synthesized films of MWCNTs-EDA/DETDA with the use of ethylenediamine and diethyyltoluenediamine [8], films with the addition of metal ions [9], films based on aminopolymers [10] etc.. In this talk, a simple method for the formation of films of oxidized CNTs was proposed as a way to simplify the process. A comparative analysis between single-walled and multi-walled CNT films was carried out. Also assumptions about the mechanical, physical and chemical properties of films from oxidized CNTs were made, which was subsequently confirmed by experiments and described in this talk.

2. Technology of the experiment
For the study, films with single-walled and multi-walled CNTs were made by oxidation and vacuum filtration of the solution with subsequent drying.

2.1. Oxidation of CNTs
At first, 5 mg of single-walled and multi-walled CNTS were taken separately for CNT oxidation. Further, nanotubes were treated separately in a mixture of 45 ml sulfuric (H₂SO₄) and 15 ml nitric (HNO₃) acids in an ultrasonic bath for 4 hours.

2.2. Vacuum filtration
The film was obtained by vacuum filtration using PTFE filter with a pore size of 45 microns. For this purpose, a standard vacuum filter unit with a connected membrane vacuum pump was used. After deposition of carbon nanotubes PTFE filter was dried at 70 °C for 10 minutes.

The obtained samples were then examined using the ATR-prefix of the Nicolet iS50 IR spectrometer. Some physical, chemical and electrical properties of the obtained films were also investigated.

3. Experimental results
After oxidation of CNTs, the solution acquired a distinctive deep black color and the dispersion of the solution became homogeneous (figure 2). In comparison with the solution of pristine CNTs (figure 1), oxidized nanotubes are more stable in water and organic solvent solutions.

The films obtained from oxidized CNTs (figure 3) have a thin, dense black structure with a resistance of 24.8 Ohm/cm, which indicates a high density and quantity of deposited nanotubes.

The mechanism of film formation is related to the ability of carboxyl groups to form hydrogen bonds as a result of delocalization of electron clouds. The energy of the hydrogen bond between oxygen and hydrogen is 132 kJ/mol, which is much more than the energy of the van der Waals interaction (10-20 kJ/mol). Hydrogen of the carboxyl group (–COOH) and oxygen of the carbonyl group (–C=O) interact with each other as a result of convergence during vacuum filtration, forming a weak intermolecular bond (figure 4).

So obtained CNT films have high chemical and thermal resistance. These films (unlike pristine CNTs) without the use of ultrasonic treatment do not dissolve in water, organic and inorganic solvents, in acids are limited to dissolve. Also, these CNT films have hydrophobic properties and are not wetted with water. It should be noted that the films have a different density depending on the type of nanotubes - multi-walled CNTs have a lower density than single-walled, which affects the speed of their subsidence: the deposition rate of multi-walled CNTs is generally faster.
A significant drawback of these CNT films is that these films have low resistance to mechanical stress. This is mainly due to the low strength of hydrogen bonds, due to which CNTs are connected to each other in the film. In should be noted that these mechanical properties are the same for both films regardless of whether film based on singlewalled or multiwalled CNTs. It follows that the strength of the material based on CNT depends primarily on the nature and strength of the chemical bond formed between the functional groups present on the surface of the nanotube (it also includes the method of forming a connection between CNTs), and then on the type of CNTs. In spite of this, it was possible to obtain a film size of about 4×2 cm² with a PTFE filter size of 5×5 cm².

To analyze the spectrum of oxidized CNT films, films based on singlewalled CNTs were compared with pristine singlewalled nanotubes (figure 5). The oscillation levels of 2900 cm⁻¹ and 2800 cm⁻¹ correspond to carbon fluctuations in the sp² and sp³ hybridization states. The spectrum corresponds to the states of carbon atoms, in which electron clouds are delocalized in hexagonal cells to form e⁻-unpaired electrons. The same peaks can be observed on the spectrum of pristine carbon nanotubes. Peak of 1800 cm⁻¹ corresponds to the oscillation of the carbonyl group (–C=O). This peak is absent in the spectrum of pristine CNTs, because it is the result of the functionalization of CNTs by acids. The oxygen of the carbonyl group forms a double bond with the carbon of the functional group. In addition, because of its greater electronegativity, oxygen is involved in the formation of hydrogen bonds in the film. The oscillation at the level of 1600 cm⁻¹ corresponds to the deformation vibrations C=C of the bond. This oscillation is also present in the spectrum of pristine CNTs, so it can be concluded that the source of the oscillation is the crystal lattice of the carbon nanotube itself. Deformation vibrations –O–H– correspond to the peak of 1300 cm⁻¹. This peak is absent in the spectrum of pristine CNTs and indicates the formation of a carboxyl group.

The spectra of multi-walled CNT films and pristine nanotubes were also analyzed using an IR spectrometer (figure 6). Their spectra are different from each other and from the spectra of single-walled CNTs and films based on single-walled CNTs. The oscillation level of 3000 cm⁻¹ corresponds to the valence oscillations of hydroxyl groups. Approximately at the level of 2900 cm⁻¹ and 2800 cm⁻¹
fluctuation of carbon atoms in the state of sp² and sp³ hybridization is observed. At the level of 1200 cm⁻¹ there is a two-humped peak, which is absent in the spectrum of pristine multi-walled CNTs (MWCNT).

![Figure 5. Comparison of IR-spectrums of single-walled CNTs and films of oxidized single-walled CNTs.](image)

Figure 5. Comparison of IR-spectrums of single-walled CNTs and films of oxidized single-walled CNTs.

![Figure 6. The IR spectrum of the MWCNT and films of MWCNT-COOH.](image)

Figure 6. The IR spectrum of the MWCNT and films of MWCNT-COOH.

The films were investigated for exposure to high temperatures. It was observed that under local heating to 420 °C film was not deformed and degraded. It was also noted that the film reacts to changes in ambient temperature, as well as reacts to IR radiation with a power of 1 watt. In this case, the film resistance drops by about 10%. It can be concluded that the films exhibit the properties of semiconductors, and such films can be used as bolometric detectors of IR radiation.

4. Conclusion
As a result, films on oxidized single-wall and multi-wall CNTs were obtained. The similarities and differences in the properties of these films, their advantages and drawbacks were shown. We can conclude that these CNT films may have limited use due to their low resistance to mechanical stress that could be further solved by using additional structuration.

5. References
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