Modification of carbon nanotubes by an ion beam of argon

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Abstract. By Scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy has been studied the effect of an argon ion beam with energy of 5 keV and various fluences (1·10¹⁶ and 5·10¹⁶ ion/cm²) on the morphology, structure, and chemical state of multi-walled carbon nanotubes (MWCNTs). It has been established that irradiation of MWCNTs with argon ions leads to the formation of structural defects and functional oxygen-containing groups of various types (hydroxyl, carboxyl / carbonyl, ether, etc.). It is shown that an increase in the fluence of the beam leads to an increase in the number of functional groups fixed on the walls of the MWCNTs, without changing the types of oxygen-containing groups. It is shown that modification by ion-beam action is promising for increasing the chemical activity and changing the electronic properties of the outer walls of MWCNTs.

1. Introduction

At present, the development of new materials based on multi-walled carbon nanotubes (MWCNTs), including composites on the based MWCNTs and metals or polymers [1], is of great interest in the field of materials science. MWCNTs possess high mechanical properties, low resistance and high thermal conductivity, as well as high specific surface area, which provides enhanced characteristics of composites based on them. However, MWCNTs obtained in industry and laboratory conditions are chemically inert, which can lead to a deterioration in the performance characteristics of materials based on them, due to the weak interaction between the components of the composites. The increase in the chemical activity of the MWCNTs surface is most often achieved by the pre-functionalization of carbon nanotubes using methods based on treatments in various corrosive media (in acids (H₂SO₄, HCl) and their mixtures) due to the formation of structural defects and the attachment of various functional groups [2]. Another way to increase the activity of the MWCNTs surface is to introduce various structural defects (vacancies, vacancy clusters, adatoms, etc.) using charged particle beams [3, 4]. In this case, ion irradiation, as a rule, is realized under vacuum conditions, which ensures high purity of the process, is more controllable and eliminates additional manipulations (rinsing in distilled water to remove oxidant residues, drying, etc.).

In this work, a study was made of the changes in the morphology, local atomic structure, and chemical state of the MWCNT surface due to the action of ionic beams of argon with various fluence using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS).

2. Experimental details

The MWCNTs arrays were synthesized using catalytic gas-phase chemical deposition on Si/SiO₂ substrates through the pyrolysis of a mixture of acetonitrile and ferrocene (100:1) at 800 °C. The
synthesis was continued for 15 min. The average thickness of the grown MWCNTs arrays was ~ 12 ± 1.2 μm. The average diameter of the initial carbon nanotubes is ~ 40 nm.

Modification of MWCNTs was carried out by a beam of argon ions with an average energy of 5 keV using an ion implantation equipment. The beam fluence was 1·10^{16} and 5·10^{16} ion/cm². The pressure of the residual gases upon irradiation was ~ 10^{-4} Torr.

The study of the morphology of the MWCNTs arrays was carried out using the scanning electron microscope JEOL JSM 6610 LV in the center of collective use of Omsk research usage center of SB RAS.

The analysis of the local atomic structure and chemical state of MWCNTs was carried out using XPS and NEXAFS methods on the equipment of the RGL station of the BESSY II synchrotron storage (Berlin, Germany). The survey XPS spectra were recorded at a photon energy of 850 eV. NEXAFS C K-edge spectra of the carbon were recorded in the leakage current measurement mode at an energy monochromator resolution of not worse than ~ 0.1 eV. For the normalization of NEXAFS spectra, the procedure of dividing the detected signal by the current measured from a plate of pure gold was used. Measurements of XPS and NEXAFS spectra were carried out in ultrahigh vacuum at a residual gas pressure in the measuring chamber of ~ 10^{-10} Torr.

3. Results and discussion

3.1. SEM data
Figure 1 shows SEM images of the surface of the initial and irradiated MWCNTs arrays. As can be seen (Figure 1a), the surface of the array of initial MWCNTs consists of curved and intertwined carbon nanotubes with an external diameter of 20 to 60 nm. Irradiation with argon ions leads to morphological changes with respect to the initial MWCNTs. There is a consolidation of MWCNTs in the surface layer of the arrays, welding of individual nanotubes into beams with the formation of new structural forms on their surfaces, and an increase in the outer diameter of nanotubes to 100 nm. These changes in the morphology of the surface layer are associated with an increase in the chemical activity of the MWCNTs surface due to the ionic stimulated formation of point and extended defects. An increase in the degree of MWCNTs crystal structure defectiveness leads to the interaction of the outer walls of individual carbon nanotubes with each other. At the same time, an analysis of the SEM images of irradiated MWCNTs allows us to conclude that the MWCNTs are sufficiently uniformly functionalized in the surface layer of the array under the influence of ion irradiation. Comparative analysis of Figures 1b and 1c allows us to conclude that an increase in the radiation dose from 1·10^{16} to 5·10^{16} ion/cm² leads to a stronger change in the morphology of the MWCNTs array and, consequently, more significant functionalization of individual nanotubes.

3.2. XPS data
Figure 2 shows the survey XPS spectra of MWCNTs before and after irradiation with an ion beam with different fluences. As can be seen, all the spectra contain carbon lines C 1s (~ 285 eV) and Auger transitions C KLL (~ 590 eV), oxygen O 1s (~ 533 eV) and Auger transitions O KLL (~ 343 eV), nitrogen N 1s (~ 401 eV). An analysis of the XPS spectra of irradiated MWCNTs showed a significant increase in the intensity of the O1s oxygen lines compared to the initial carbon nanotubes, which indicates the oxidation of the surface of carbon nanotubes. The quantitative data obtained from the analysis of the XPS spectra show that after irradiation with argon ions, the oxygen content on the MWNT surface increases to ~8-11 at.% (Table 1). The high oxygen content is associated with the formation of point and extended structural defects, dangled chemical bonds and adatoms on the outer walls of MWCNTs as a result of irradiation. Further contact of irradiated samples with the atmosphere leads to the formation of functional oxygen-containing groups of different composition on the surface of MWCNTs.
Figure 1. SEM images of the MWCNTs arrays: (a) – initial, (b) – irradiated with a fluence of $1 \cdot 10^{16}$ ion/cm$^2$ and (c) – irradiated with a fluence of $5 \cdot 10^{16}$ ions/cm$^2$
Figure 2. Survey XPS spectra of the MWCNTs arrays: (a) – initial, (b) – irradiated with a fluence of $1 \cdot 10^{16}$ ion/cm$^2$ and (c) – irradiated with a fluence of $5 \cdot 10^{16}$ ions/cm$^2$.

Table 1. The concentration of elements for MWCNTs irradiated with various fluence

| Samples                      | Concentration (at %) |
|------------------------------|----------------------|
| MWCNTs                       | 96.5 2.2 1.3         |
| Irradiated with fluence $1 \cdot 10^{16}$ ion/cm$^2$ | 90.2 1.6 8.2     |
| Irradiated with fluence $5 \cdot 10^{16}$ ion/cm$^2$ | 87.5 1.4 11.1 |

3.3. NEXAFS data

To study the changes in the local atomic structure of MWCNTs and the composition of the functional groups formed as a result of irradiation, the NEXAFS method was used. The analysis was carried out from the absorption spectra of the K-edge of carbon, which characterizes the transitions from the core level C1s to free states $\pi^*$-$2p_z$ and $\sigma^*$-$2s$-$2p_{x,y}$ of the conduction band state [5, 6].

In the C K-edge absorption spectrum of the initial MWCNTs (Fig. 3, curve 1) there are the intense and narrow $\pi^*(C=C)$ resonance for the photon energy of $\sim 285$ eV and $\sigma^*(C=C)$ resonance with two local maxima at the photon energy $\sim 292$ and $\sim 293$ eV, which indicates a low defect in the structure of the MWCNTs walls [7]. The presence of resolved local maxima at photon energies of $\sim 303$ and $\sim 307$ eV also indicates a high degree of ordering of carbon in the graphene walls of MWCNTs [7].

In the C K-edge XANES spectra of the irradiated MWCNTs, significant changes are observed (Fig. 3, curves 2 and 3) compared to the spectrum of the initial MWCNTs. A decrease in the intensity of the $\pi^*(C=C)$ resonance and the shift of its maximum towards low photon energies are noted. In addition, there is a decrease in the fine structure of the $\sigma^*(C=C)$ resonance: local maxima at photon energies of $\sim 293$ and $\sim 293$ eV are not resolved, as well as a decrease in the intensity and also smearing of the spectrum structure in the high-energy region (300-308 eV). These changes indicate significant distortions of the crystal structure of sp$^2$-carbon, partial amorphization of the MWCNTs walls, and the presence of number of carbon atoms in sp$^3$-hybridization. In the absorption spectra of
irradiated MWCNTs, additional maxima $a_1$, $a_2$, $a_3$ located between $\pi^*(C=C)$ and $\sigma^*(C=C)$-resonances are also observed, which indicates the oxidation of carbon nanotubes with the formation of oxygen-containing groups of different composition [8–10]. The maximum $a_1$ at photon energy ~ 286 eV corresponds to $\pi^*(C-OH)$ states of carbon in the composition of hydroxyl and phenolic groups [8–10]. The maximum $a_2$ at the photon energy ~ 288 eV corresponds to $\pi^*(C=O)$ carbon in the carboxyl and carbonyl groups. The states $a_3$ at the photon energy ~ 290 eV correspond to carbon in the $\sigma^*(C-O)$ bond in epoxy and ether groups [8-10].

A comparative analysis of curves 2 and 3 in Figure 3 showed that an increase in the beam fluence from ~ 1·10$^{16}$ to ~ 5·10$^{16}$ ions/cm$^2$ leads to an increase in the amount of carbon chemically bonded to oxygen in the MWCNTs walls. However, the composition of the functional groups formed for different fluence is identical. This allows us to say that the number of functional groups fixed on the MWCNTs surface directly depends on the beam fluence i.e. on the concentration of the formed structural defects.

The oxygen-containing groups which formed on the MWCNTs surface as a result of irradiation are active sites for fixing metal particles, their oxides and polymers in the formation of composites based on carbon nanotubes [11].

![Figure 3. NEXAFS C K-edge spectra of the MWCNTs arrays: (a) – initial, (b) – irradiated with a fluence of 1·10$^{16}$ ion/cm$^2$ and (c) – irradiated with a fluence of 5·10$^{16}$ ions/cm$^2$.](image)

4. Conclusion
Effect of argon ion beam irradiation with various fluences on the morphology, local structure and chemical state of MWCNTs were studied by using the SEM, XPS and NEXAFS methods. It has been established that irradiation with a continuous beam of argon ions leads to radiation-stimulated formation of a large number of defects, distortions of the MWCNT crystal structure, and carbon oxidation with the formation of various types of functional oxygen-containing groups. In this case, as the beam fluence increases, the number of functional groups fixed on the MWCNTs walls increases, without changing the types of oxygen-containing groups. The obtained results showed that the use of the argon ion beam is a promising method for modification that allows the surface layers of the MWCNTs arrays to be functionalized by creating structural defects and fixing functional groups of
different composition. In the future the proposed modification method can be used to direct change the electronic properties of MWCNTs, as well as to improve interfacial adhesion in composites.

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