Electrical properties of irradiated individual multi-walled carbon nanotubes after gas adsorption

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Abstract. The electrical parameters of individual nitrogen-doped carbon nanotubes (irradiated by electrons, protons, and argon ions) were determined during the ammonia and nitrogen dioxide exposure using the methods of scanning probe microscopy.

1. Introduction
Carbon nanotubes (CNTs) present excellent properties when used as sensing materials, supercapacitors, and others [1]. The contribution of nitrogen doping for CNTs enhances electrical conductivity, and nitrogen-containing defects serve as anchoring sites for specific gas molecules. In order to change electrical properties and create adsorption centres in nitrogen-doped CNTs, it is necessary to functionalize them, for example, by electron or ion irradiations [2]. Irradiation of doped nanotubes leads to the formation of adsorption centres that makes it possible to use them in sensory nanoelectronic.

Individual CNTs are ideal materials for nanodevices manufacturing but electrical measurements of a single nanotube are extremely difficult. Scanning probe microscopies techniques allows to get information about electrical properties individual nanoobjects with high resolution.

In the present work, electrostatic force microscopy (EFM) and conductive atomic force microscopy (C-AFM) have been successfully used for determining the free carrier concentration and the electrical conductivity in individual CNTs (irradiated by electrons, protons, and argon ions) during adsorption of oxidative and reductive gases.

2. Material and methods
Synthesis of CNTs was described in Ref. [3]. CNTs were irradiated by various beams: electrons (with energy 3 MeV and doses $10^{16}$ cm$^{-2}$), protons (140 keV, $10^{14}$ cm$^{-2}$), and argon ions (15 keV, $10^{16}$ cm$^{-2}$). The samples for the investigation were single CNTs deposited on structures with gold electrodes [3].

Conductivity and carrier concentration measurements were performed on the atomic force microscope MFP-3D SA (Asylum Research) using C-AFM and EFM methods [3]. The conductivity of CNTs was calculated according to the lengths and outer diameters of CNTs obtained from first pass EFM-images.

Scanning probe microscopy (SPM) measurements of individual CNTs were carried out in nitrogen atmosphere with reducing and oxidizing gases. Changes in the electrical properties of CNTs during ammonia and nitrogen dioxide adsorption at a concentration of 1000 ppm were studied.
3. Results and discussion

Figure 1 presents typical values and range of the conductivity of as-grown and irradiated CNTs in dry nitrogen atmosphere and after ammonia and nitrogen dioxide adsorption. Inset on Figure 1 presents a first pass of EFM image visualizing CNT, which lays between two neighbouring electrodes.

Figure 2 shows the free carrier concentration of as-grown and irradiated CNTs in dry nitrogen atmosphere and after exposure to ammonia and nitrogen dioxide. Ammonia molecules (reductive gas) adsorbed on CNTs act as electron donors to the nanotubes, which lead to increase of conductivity and electron concentration. With adsorption of acceptor molecules (nitrogen dioxide), conductivity and electrons concentration of doped CNTs decrease.

The type of irradiation particles effects on conductivity and carrier concentration in individual CNTs. Irradiated CNTs have a variety of charge carriers due to the kind and concentration of irradiation-induced defects in CNT walls. A change in conductivity of irradiated CNTs correlates with a change in charge carrier concentration in CNTs under adsorption of ammonia and nitrogen dioxide molecules.

Exposure to nitrogen dioxide increases the hole concentration in CNTs irradiated by protons and argon ions, because the extracted electrons by oxidizing gas molecules result in the generation holes in the valence band. Conductivity of these CNTs increases because the majority charge carriers are holes. The conductivity of the p-type CNTs under exposure to reducing gas (ammonia) decreases because generated electrons recombine with holes.

In CNTs irradiated by electrons, the majority charge carriers are electrons. Adsorption of nitrogen dioxide leads to a change of the majority charge carriers. As a result, holes concentration is more than the electron concentration in the CNTs before to nitrogen dioxide adsorption, so the conductivity increases. Exposure to reductive gas (ammonia) increases the electrons concentration in CNTs irradiated by electrons, and therefore the conductivity increases. Since the Fermi level shift during adsorption of the oxidative and reductive gases slightly changes, the concentrations of the majority charge carriers are practically equal, but they are opposite in sign. Therefore, C-AFM results show that the electrical conductivity of CNTs irradiated by electrons increases during adsorption in both gases.

Figure 1. Mean values and range of electrical conductivity of individual nitrogen-doped CNTs (as-grown and irradiated by electrons, protons, and argon ions) during adsorption of ammonia and nitrogen dioxide molecules. Inset: 3D first pass of EFM image of individual CNT on gold electrodes.
Figure 2. Mean values of free carrier concentration in individual doped CNTs (as-grown and irradiated by electrons, protons, and argon ions) during adsorption of ammonia and nitrogen dioxide molecules. Inset: EFM image of individual CNT at tip bias +5V.

4. Conclusion
Combination of two techniques of scanning probe microscopy (C-AFM and EFM) allows getting values of conductivity and carriers concentration of individual CNTs after gas exposition. The dependence of the change in conductivity of irradiated CNTs is due to the type of majority charge carriers. Using an independent measurement of conductivity and charge carrier concentration, it is possible to determine the change in mobility in CNTs after irradiation.

Irradiation of CNTs produces defects that decreases conductivity (by an order of magnitude) and creates molecular centres of adsorption. These centres can be used in composite structures for binding with additional components.

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