Electrical properties of irradiated individual multi-walled carbon nanotubes at gases adsorption

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Carbon nanotubes (CNTs) present excellent properties when used as sensing materials, supercapacitors, and others [1]. The contribution of nitrogen doping for carbon nanotubes enhances electrical conductivity and nitrogen-containing defects serve as anchoring sites for specific gas molecules. For improve electrical properties of nitrogen-doped CNTs is a need to functionalize them, for example, by electron or ion irradiations [2].

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 present work electrostatic force microscopy (EFM) and conductive atomic force microscopy (C-AFM) successfully have been 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.

Samples preparation, measurements and calculations the electrophysical parameters were described in [3]. The change the electrical properties of CNTs during ammonia and nitrogen dioxide adsorption at a concentration of 1000 ppm were studied.

Figure 1 presents typical values the conductivity of as-grown and irradiated CNTs in dry nitrogen and after ammonia and nitrogen dioxide adsorption.

Figure 2 shows the free carrier concentration of as-grown and irradiated CNTs in dry nitrogen and upon exposure to ammonia and nitrogen dioxide.

Ammonia molecules (reductive gas) adsorbed on CNTs act as electron donors to the nanotubes, which led to increase of conductivity and electron concentration. With adsorption of acceptor molecules (nitrogen dioxide) conductivity and electrons concentration of doped CNTs decreases.



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 AFM image of individual CNT on gold electrodes.



Figure 2. Mean values and range of free carrier concentration in individual doped CNTs (asgrown 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.

The type of irradiation particles effects on conductivity and carrier concentration in individual CNTs. Irradiated CNTs have various majority 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 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 is slightly change, 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.

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 force microscopy.

- 1. T.S. Williams, N.D. Orloff, J.S. Baker et al., ACS Appl. Mater. Interfaces 8, 9327 (2016).
- 2. J.-J. Adjizian, R. Leghrib, A.A. Koos et al., Carbon 66, 662 (2014).
- 3. D.V. Sokolov, N.A. Davletkildeev, V.V. Bolotov et al., *IOP Conf. Series: Materials Science and Engineering* **256**, 012018 (2017).