Combination of scanning probe microscopy techniques for evaluating the electrical parameters of individual multiwalled carbon nanotubes

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Abstract. Using two techniques of scanning probe microscopy, the electrical properties (work function, Fermi level position, free carriers’ concentration, electrical resistance, conductivity, and carriers’ mobility) of individual multiwalled carbon nanotubes were evaluated.

1. Introduction
Carbon nanotubes (CNTs) with unique electrical properties are considered as promising materials for nanoelectronics [1]. Nitrogen doping is an effective way of modifying the electrical properties of CNTs [2], because the nitrogen atoms generate the defects in CNT walls.

For development of the devices consisting of single nanoscale objects (such as nanotubes, nanowires, and nanoparticles), it is necessary to study their properties. Scanning probe microscopy (SPM) is an effective way to obtain information about the properties of individual CNTs [3]. The combination of several SPM methods allows obtaining a complete set of electrophysical parameters of CNTs.

In this work, we evaluate electrophysical parameters of individual undoped and nitrogen-doped multiwalled CNTs based on electrostatic force microscopy (EFM) and conductive atomic force microscopy (C-AFM). To study the change in the electrical properties of CNTs during gas adsorption, SPM measurements of doped CNTs exposed to ammonia (reducing agent) and nitrogen dioxide (oxidizer) gases were carried out.

2. Material and methods
2.1. Multiwalled carbon nanotubes
Chemical vapor deposition (CVD) method was used for synthesis of CNTs. Undoped and nitrogen-doped multiwalled CNTs were grown on SiO₂/Si substrates from pyrolysis of toluene and acetonitrile, respectively. Fe-particles formed by ferrocene decomposition in the synthesis zone at 850°C served as a catalyst for nanotube growth. According to X-ray photoelectron spectroscopy, the nitrogen content in doped CNTs was 3.7 at.%

The samples for the measurements were CNTs deposited on comb-shaped arrays of gold electrodes. Structures with gold contacts were photolithographically formed on a 130 nm thermally grown SiO₂ layer on the n-Si wafer with electrical resistivity 0.1 Ω·cm. CNTs were deposited on gold electrodes from a suspension after ultrasonic dispersion in dichloromethane for 1 hour.
2.2. Electrical measurements

Individual CNTs lying on two adjacent gold contacts were revealed using AFM-scanning. I-V curve measurements were performed by C-AFM; mean value and range of the longitudinal electrical conductivity of CNTs were determined. Considering the length and outer diameter of CNTs obtained from AFM-images the specific conductivity of CNTs was calculated.

The Fermi level shift in CNTs was estimated using EFM. The measurements were made in the region between the two gold contacts, where the single nanotubes lay on the SiO₂ surface. SPM measurements were performed by the atomic force microscope MFP-3D SA (Asylum Research) in air and in nitrogen atmosphere with reducing (ammonia) and oxidizer (nitrogen dioxide) gases.

3. Results and discussion

Inset in Figure 1 shows the example of the 3D AFM image of a nanotube with diameter 8 nm located between the two adjacent gold electrodes.

The current–voltage curves of Au-CNT-Au structures at voltages from -1 to +1 V have a linear shape. The slope of I–V curve was used to determine the longitudinal electrical resistance of the CNTs on metallic contacts. Resistance of individual CNT was calculated by method considering the contact resistance between nanotube and gold [4]. Figure 1 shows calculated specific conductivity of individual CNTs using the AFM image data for diameter and length of the CNTs. The cross section of the outer wall of nanotube was taken as the cross-sectional area for specific conductivity.

Based on EFM images (Fig. 2, inset), mean value of work function (WF) in CNTs was measured as shown in [5]. For reference, the mean values of WF in undoped and doped CNTs (Fig. 2) and mean values of Fermi level shift were determined, and the carrier concentration of CNTs was calculated (Table 1). The concentration and conductivity values were used to calculate the carrier mobility. In the Table 1 all the electrical parameters of CNTs are presented.

According to the data in Table 1, the conductivity of N-doped CNTs is more than the one of undoped CNTs. This is due to electrically active nitrogen-containing defects, which increase the carrier concentration in doped CNTs and the concentration of electron scattering centers. Therefore, the carrier mobility in doped CNTs is less than in undoped ones.

Figure 1. Mean values and range of the longitudinal electrical conductivity of undoped and N-doped CNTs. Inset: 3D AFM image of CNT on gold electrodes.

Figure 2. Mean values and range of the work function of undoped and N-doped CNTs. Inset: AFM (left) and EFM (right) image of CNT.
Table 1. Mean value and range of electrical parameters of the individual undoped and N-doped CNTs.

| Parameters                  | The average value and range |
|-----------------------------|-------------------------------|
|                            | Undoped CNT                  | N-doped CNT                  |
| Resistance, Ω · cm         | 9.7·10^{-3}±3.8·10^{-5}      | 5.4·10^{-4}±2.0·10^{-5}     |
| Conductivity, S/cm          | 10.3·10^{3}±4.0·10^{3}       | 18.6·10^{3}±7.0·10^{3}      |
| Work function, eV           | 4.7±0.11                     | 4.5±0.12                    |
| Charge carriers concentration, cm^{3} | 7.9·10^{18}±2.8·10^{18}     | 3.2·10^{19}±1.1·10^{19}     |
| Mobility, cm^{2}/(V·s)     | 8.16·10^{3}±3.2·10^{3}       | 3.6·10^{4}±0.3·10^{3}      |

The change in the electrophysical parameters of nitrogen-doped CNTs during the adsorption of molecules of the reducing gas (NH_{3}) and oxidizing gas (NO_{2}) at concentration of 1000 ppm was studied (Fig. 3) using presented techniques.

When the reducing gas is adsorbed, the Fermi level shift in doped CNTs increases insignificantly (Fig. 3), which may be due to acceptor-like defects in the CNTs walls. In the case of adsorption of the oxidizing gas, the Fermi level shift is substantially reduced (Fig. 3), which indicates the dominance of donor-like defects in the walls of CNTs, in accordance with the type of dopant.

4. Conclusion

The electrical parameters of individual undoped and nitrogen-doped CNTs were obtained using a combination of conductive atomic force microscopy and electrostatic force microscopy techniques. It was shown that the nitrogen, being a donor impurity for CNTs, provided excess concentration of electrons. This leads to an increase of the Fermi level position and a decrease of the work function in doped CNTs.

The electrical conductivity and the Fermi level shift during the adsorption of ammonia and nitrogen dioxide were measured for nitrogen-doped CNTs. The increase and decrease in the average value of the conductivity correlate with increase and decrease of Fermi level position leading to a change of carrier concentration in the outer walls of multiwalled CNTs.

![Figure 3](image-url). Mean values and range of electrical conductivity (on the left) and mean Fermi level shift (on the right) in individual doped CNTs during adsorption of ammonia and nitrogen dioxide molecules.
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