Gas sensing properties of individual composite nanostructures TiO$_{2-x}$/MWCNT and SnO$_{x}$/MWCNT measured by scanning probe microscopy

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Abstract. The gas sensitivity properties of individual composite nanostructures based on multi-walled carbon nanotubes (MWCNT), functionalized by argon ions and coated with tin and titanium oxides, were investigated by the methods of scanning probe microscopy. The Fermi level shift and the change in longitudinal conductance of nanostructure upon absorption of ammonia and nitrogen dioxide are determined. It is shown that the change in conductance of the composite nanostructures correlates with the Fermi level shift under gases exposure as a result of charge carrier concentration changing in the metal oxide surface layers upon adsorption of gas molecules.

1. Introduction
Composite materials based on multi-walled carbon nanotubes (MWCNT) and metal oxides are promising materials for various applications in nanoelectronics [1], in particular, for gas-sensing elements [2]. The trend of miniaturization of electronic devices and the fundamental replacement of massive layers by nanoscale elements attracts a great interest in the study of electron transport processes in individual nanostructures. For study of these processes, the methods development for measuring the electrical parameters of individual nanostructures is needed. Scanning probe microscopy is an effective method to study the electrical properties of single nanostructures, for example, conductive atomic force microscopy (C-AFM) and electrostatic force microscopy (EFM) [3-5].

In this work, the electrical conductivity of individual MWCNTs and metal oxides/MWCNT nanocomposites was determined by the C-AFM method. The work function of MWCNTs and metal oxides/MWCNT nanocomposites was measured using EFM, and then the Fermi level shifts in these nanostructures were found. The gas-sensing properties of the nanostructures were studied by the change in conductivity and the Fermi level shift under the exposure to a reducing and an oxidizing gas.

2. Materials and methods
MWCNTs synthesized by chemical vapour deposition were studied. According to X-ray photoelectron spectroscopy data, the nitrogen concentration in nanotube walls is 3.7 at%. The functionalization of as-grown MWCNTs was carried out by argon ions irradiation with energy 5 keV and dose $10^{16}$ cm$^{-2}$. The composite nanostructures of metal oxide/MWCNTs were fabricated by deposition of non-stoichiometric titanium dioxide (TiO$_{2-x}$) and tin oxide (SnO$_x$) on the surface of functionalized MWCNTs using magnetron sputtering [6,7].
Figure 1. AFM images of individual composite nanostructures located on two adjacent gold microelectrodes: (a) TiO$_2$/MWCNT and (b) SnO$_x$/MWCNT.

Individual MWCNTs, TiO$_2$/MWCNTs, and SnO$_x$/MWCNTs were deposited on gold microelectrode array from suspensions by spin coating. The suspensions of nanotubes and nanostructures were obtained by ultrasonic dispersion of their layers in dichloromethane for 20 min. C-AFM and EFM measurements were performed using an atomic force microscope MFP-3D SA (Asylum Research) with conductive cantilevers HA_FM/Pt (NT-MDT) in dry nitrogen (RH ~ 2%) at room temperature. Gas sensing properties were investigated on exposure to a reducing gas (ammonia) and an oxidizing gas (nitrogen dioxide) with concentrations of 1000 ppm.

3. Results and discussion

Optical and atomic-force microscopes were used to detect the individual MWCNTs and composite nanostructures located on two adjacent electrodes (Fig. 1). The work function of individual nanoobjects, placed between the electrodes on SiO$_2$ surface, was determined by the technique described in [8]. The mean values of the Fermi level shift for obtained samples upon adsorption of ammonia and nitrogen dioxide were calculated from the values of the work function (Fig. 2).

The work function of MWCNTs functionalized by argon ions averaged 4.86 eV, which is 0.36 eV more than non-functionalized MWCNTs (4.5 eV). By comparing the work function values for highly oriented pyrolytic graphite as calibration sample and MWCNTs, it has been found that the Fermi energy in functionalized MWCNTs is just below the Dirac point by 0.13 eV. This fact indicates that the argon ions form acceptor-like defects in nanotube walls and holes become the major charge carriers in functionalized MWCNTs. During the adsorption of the reducing gas NH$_3$ known as the electron donor [9], the Fermi level shift in MWCNTs increases slightly due to electron-hole recombination. In the case of adsorption of the oxidizing gas NO$_2$, which is an electron acceptor [10], the Fermi level shift decreases significantly caused by the increase of hole concentration in MWCNT walls.

The Fermi level shift in TiO$_2$/MWCNTs is similar to functionalized MWCNTs, but in contrast to MWCNTs, the titanium oxide formed by magnetron sputtering is n-type semiconductor and major charge carriers therein are electrons. Adsorption of a reducing gas leads to the increase in the electron concentration on the TiO$_2$/MWCNT surface and the Fermi level shifts upward. During the adsorption of an oxidizing gas, the electron concentration in TiO$_2$/MWCNT decreases, band-bending at surface increases, and the Fermi level shifts deeper in the energy gap (Fig. 2).

In the SnO$_x$/MWCNTs nanostructure the Fermi level shift during the gas adsorption is the opposite (Fig. 2). Tin oxides are a wide-gap semiconductor with band-bending near the SnO$_x$ surface due to surfaces states. This is responsible for formation of space charge region in tin oxide. It has been previously shown that SnO$_x$ obtained by magnetron sputtering is an amorphous oxide with defect structure and high density of dangling bonds on the surface [6]. As a result, a high density of acceptor-type surface states exists in the band gap of the material, which leads to the Fermi level pinning deeper in band gap and strong band bending at the SnO$_x$ surface.
After adsorption of the oxidizing gas, electrons from deep acceptor levels transfer to adsorbate energy levels. The positive charge of surface defect states, which occurs after electrons leave, can partially compensate the surface negative charge thus leading to an increase in the Fermi level shift upwards (Fig. 2). These processes can be considered for explanation of the observed effect for SnO$_x$/MWCNTs nanostructure.

The mean value and range of the conductivity for individual MWCNTs, TiO$_{2x}$/MWCNTs and SnO$_x$/MWCNTs in dry nitrogen, ammonia, and nitrogen dioxide were determined by C-AFM measurements (Fig. 3). The electrical conductivity of individual TiO$_{2x}$/MWCNTs and SnO$_x$/MWCNTs is of the same order of magnitude as that of individual nanotubes. This fact indicates the essential contribution of the MWCNT walls to the conductivity of the composite nanostructures. The conductivity change during the gas exposure is caused by change in the Fermi level shift for individual MWCNTs, TiO$_{2x}$/MWCNTs, and SnO$_x$/MWCNTs nanostructures.

A decrease and increase in the mean value of the conductivity for MWCNTs functionalized by argon ions correlate with the Fermi level shift due to variation of the hole concentration in the MWCNT walls under gases exposition.

A similar conductivity change upon gas adsorption was observed also for TiO$_{2x}$/MWCNTs nanostructures. However, TiO$_{2x}$, in contrast to nanotubes, is n-type semiconductor with electrons as the main charge carriers. Thus, during the ammonia adsorption, the Fermi level shifts upward due to an increase of the electron concentration leading to an increase in electrical conductivity of TiO$_{2x}$/MWCNTs. Conversely, the Fermi level shifts downward upon nitrogen dioxide adsorption that leads to a decrease in the conductivity of TiO$_{2x}$/MWCNTs nanostructures (Fig. 3).

For SnO$_x$/MWCNTs nanostructures, a decrease and increase in the mean value of the conductivity upon exposure to gases also correlate with a decrease and increase in the Fermi level shift as a result of a change in the charge carrier concentration in the surface layers of the metal oxide for composite nanostructures.

4. Conclusion
The Fermi level shift and the longitudinal conductivity of individual nanotubes and TiO$_{2x}$/MWCNTs and SnO$_x$/MWCNTs nanostructures upon adsorption of oxidizing and reducing gas molecules have been determined with high resolution using electrostatic force microscopy and conductive atomic force microscopy. The conductivity of the individual TiO$_{2x}$/MWCNTs and SnO$_x$/MWCNTs is very close to that of individual MWCNT indicating the essential contribution of the nanotube walls in the total conductivity of the functionalized MWCNT coated with tin and titanium oxides. It is shown that the
change of the conductivity is consistent with the Fermi level shift caused by change of the free charge carrier concentration in the surface layers of the composite nanostructures upon gas exposure.

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