Electronic structure of the „metal oxide/carbon nanotube“ interface

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The results of experimental and theoretical analysis of the structure of composites based on multi-walled carbon nanotubes (MWCNTs) and metal oxides are presented. Layers of tin and titanium oxides were formed by magnetron sputtering on MWCNT arrays with various degrees of defectiveness. The formation of metal oxide layers more uniform in morphology and structure on the surface of MWCNTs treated with an argon ion beam is shown. Modeling based on quantum mechanical calculations showed that the interaction of metal oxides with a defective carbon surface occurs with the formation of chemical bonds and a change in the electronic properties of the interface.

Keywords: carbon nanotubes, composites, tin oxide, titanium oxide, interfaces, quantum mechanical calculations.

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Composites based on nanostructured carbon (carbon nanotubes, graphene, etc.) and tin oxides, as well as titanium oxides are promising in the development of high-sensitive gas sensors and lithium-ion batteries with increased capacity [1,2]. As a rule, carbon materials have high chemical stability, which makes it difficult to obtain composites with uniform distribution and reliable fixation of metal oxides on the surface of the carbon base. This problem is solved by functionalizing the carbon material by increasing the degree of defectiveness of its crystal structure and introducing heteroatoms. For this purpose, the processing of carbon materials in various oxidizing environments is used, as well as the effect of directed energy flows (ion, electron, proton, etc. beams) [3]. Studying the features of the interaction of metal oxides with a carbon matrix at the interfaces of composites opens the possibility of obtaining materials with the required set of physicochemical properties. To carry out a correct analysis of the structure of composites containing nanostructured components, the use of a set of experimental surface-sensitive methods, as well as quantum mechanical calculations, are required.

In this paper, using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), the features of the morphology, structure and chemical state of composites with tin oxide and titanium oxide formed on the surface of MCNTs with varying degrees of surface defects were studied. Experimental data were used to model the interaction of defective carbon structure with titanium oxides and tin oxides.

To form the composites MCNT arrays were used, the arrays were synthesized on silicon substrates by catalytic vapor deposition using a mixture of acetonitrile and ferrocene (100 : 1 vol.). The outer diameter of MCNTs in the arrays was 30−70 nm. To form structural defects, part of MCNT arrays was irradiated with argon ions with an energy of 5 keV and a dose $\sim 10^{16}$ cm^{-2}. Ion treatment under these modes ensures the formation of structural defects (vacancies and vacancy clusters) and the fixation of oxygen atoms ($\sim$ 10 at.%) on the surface of carbon nanotubes in the form of various functional groups [4]. The deposition of tin oxides and titanium oxides onto substrates with initial and irradiated MCNTs was carried out using the method of magnetron sputtering of targets of metallic titanium and tin dioxide in a plasma containing a mixture of argon and oxygen. The structure and morphology of the composites were analyzed using JEOL 6610 LV electron microscope. Images were recorded at accelerating voltage of up to 20 kV. The chemical state of the composites was studied by XPS mrthod using a non-monochromatic source with Al anticathode. Simulation of the interaction of MCNT defective surface with metal oxides was carried out using quantum mechanical calculations within CASTEP code based on the generalized gradient approximation based on the Perdue–Burke–Eisernhoff potential using the plane wave method (GGA PBE for solid) [5]. The cutoff energy for the interface systems under study was equal to 1100 eV. Integration over the Brillouin zone was carried out using a grid of k-points $3 \times 3 \times 1$. The software package Material Studio 8.0 was used for calculations. MCNT surface was simulated by a flat fragment of a graphene plane. This approximation, which does not take into account the curvature of graphene walls, is acceptable when performing quantum mechanical calculations for MCNT with a diameter of more than 10 Å [6].

In the composite formed on the initial MCNTs (Figure 1, *a*), the tin oxide is distributed over the individual nanotubes surface rather nonuniformly in form of continuous layersm and globular formations with dimensions

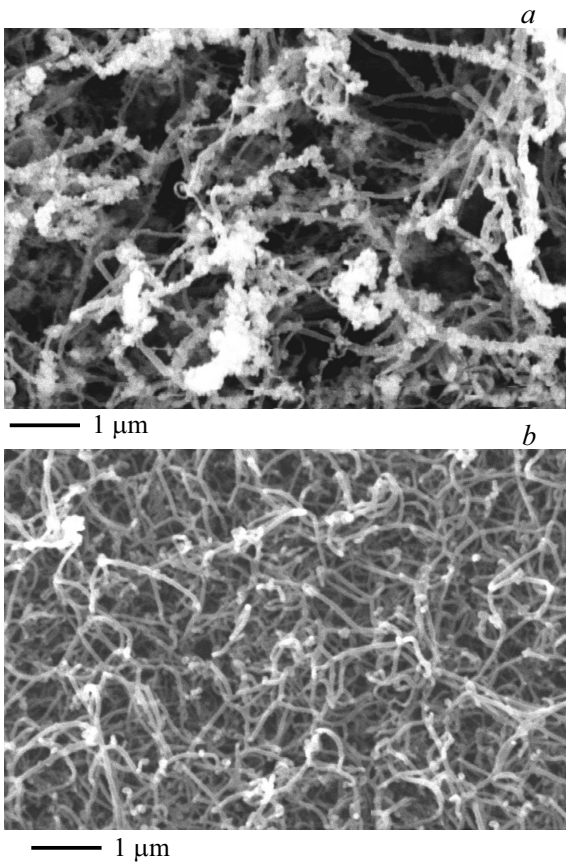

Figure 1. SEM images of SnO_x/MCNT composites formed on the original (*a*) and irradiated (*b*) MCNTs, respectively.

of ∼ 50–200 nm. In the SEM image of the composite obtained on irradiated MCNTs (Figure 1, *b*), uniform distribution of metal oxide is observed, and globules are almost completely absent. In SEM images of composites with titanium oxide (not shown in the Figures), similarly, the formation of more uniform oxide coating on the surface of irradiated MCNTs is observed. Analysis of SEM images suggests an increase in the adhesion of metal oxides to the surface of MCNTs with a higher degree of defectiveness in the structure of the outer walls. Most likely, this is achieved due to the interaction of SnO_x and TiO_x with structural defects and oxygen groups present on the surface of irradiated MCNTs.

XPS C 1s spectra of the composites under study were approximated by five components (C1–C5), which correspond to states of carbon with different chemical environments (Figure 2) [4,7]. Component C1 (bond energy 284.5 ± 0.1 eV) corresponds to the states of carbon forming the framework of carbon nanotubes (C=C bonds). Component C2 (bond energy 285.0 ± 0.1 eV) is associated with the defects presence in the MCNT walls. Components C3, C4 and C5 correspond to carbon in the composition of C–O/C–O–C, C=O and COOH bonds, respectively (bond energies ∼ 286.5, ∼ 288 and ∼ 289 eV). From Figure 2 it is clear that the intensity of the components corresponding to carbon-oxygen chemical bonds and structural defects (C2–C5) is noticeably higher in composites formed on irradiated MCNTs (spectra *2* and *4*), compared with the spectra of composites formed on the original MCNTs (spectra *1* and *3*). The most noticeable increase is observed for components C4 and C5, corresponding to carbon-oxygen groups with double bond (C=O and COOH). Previously [8], using ultrasoft X-ray absorption spectroscopy it was shown that tin oxide and titanium oxide, obtained by magnetron sputtering in the modes used in this paper, are represented by non-stoichiometric oxides with oxygen deficiency. Taking these data into account, modeling of the interaction of tin oxides and titanium oxides with the defective surface of MCNTs was carried out.

The base defect used in quantum mechanical calculations (Figure 3, *a*), was obtained by creating a divacancy in the center of the original fragment of a graphene plane containing 60 carbon atoms. Next, two oxygen molecules

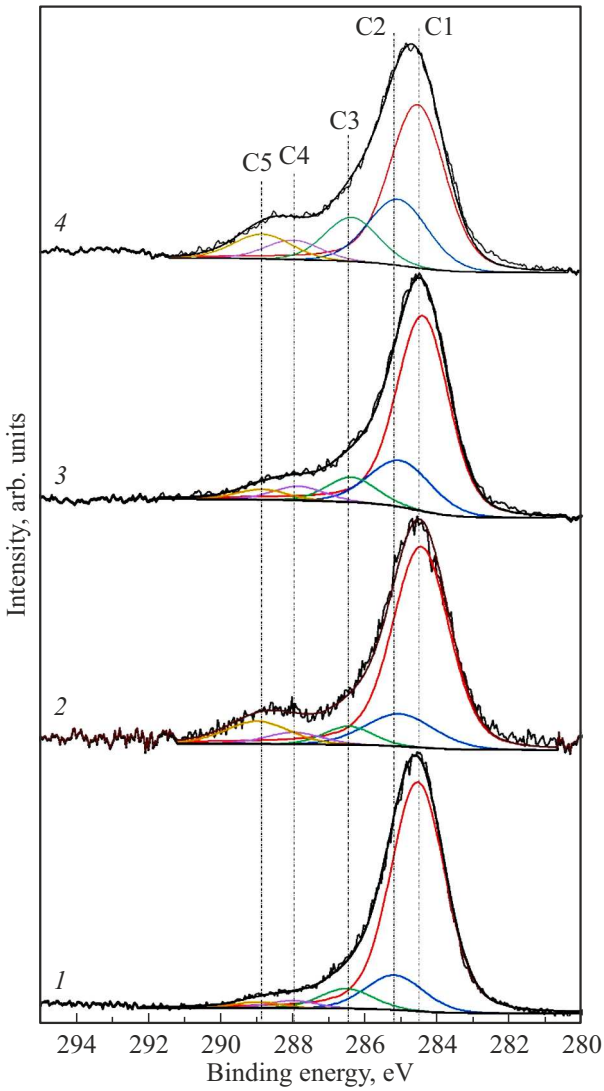

Figure 2. XPS C 1s spectra of composites TiO_x/MCNT, formed on the original (*1*) and irradiated MCNT (*2*), and composites SnO_x/MC NT formed on original (*3*) and irradiated MCNTs (*4*).

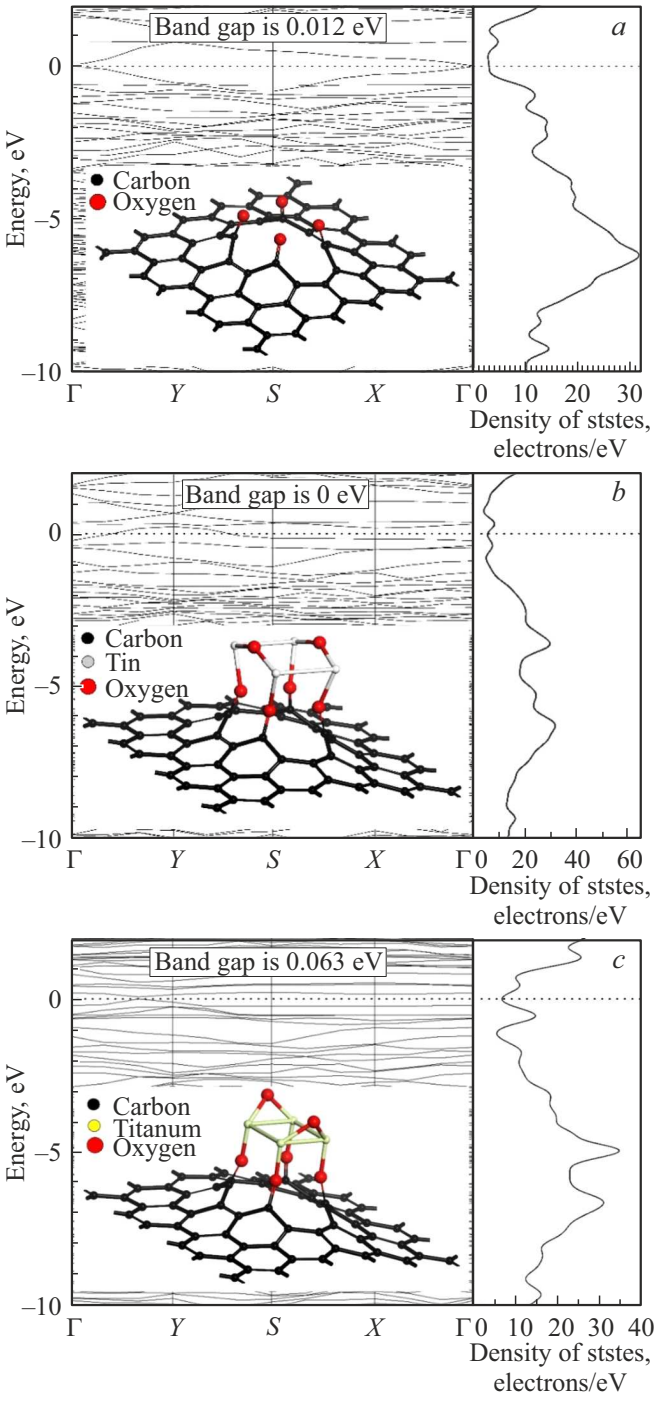

Figure 3. Band structure (left) and density of states (right) after optimization: *a* — basic defect; *b* — basic defect with tin oxide cluster; *c* — basic defect with titanium oxide cluster (inserts show optimized structures).

were added symmetrically to the resulting divacancy. At a distance of ~ 1.60 Å from the plane of the graphene cell, dissociative adsorption of O_2 molecules occurred with the formation of four oxygen atoms linked by double covalent bonds to the carbon atoms of the graphene cell. Calculations showed that the total energy of the system after the formation of four C=O bonds decreases by 7.948 eV, which indicates the thermodynamic stability of the base defect. Analysis of the density of states near the Fermi level showed that the electronic properties of the graphene cell with a defect change — the presence of a band gap 0.012 eV is observed.

Nonstoichiometric oxides of tin and titanium (SnO_x and TiO_x) were simulated as clusters containing 4 metal atoms and 2 oxygen atoms. After adding clusters to the base defect, bonds are formed between metal atoms and oxygen atoms, which are fixed on the defective graphene surface (Figure 3, *b* and *c*). The formation of the four specified bonds leads to a significant decrease in the total energy of the systems. The energy per bond formed is 1.170 eV in the case of SnO_x cluster and 2.547 eV in the case of TiO_x cluster, which indicates a chemical interaction. Calculation of the density of states near the Fermi level showed that the band gap for the structure with titanium oxide (Figure 3, *c*) increases relative to the base defect and amounts to 0.063 eV. For the structure with tin oxide there is no band gap, which indicates metallic properties (Figure 3, *b*).

Thus, using experimental and theoretical methods, the analysis of the electronic and atomic structure at the metal oxide/carbon nanotube interfaces in composites with tin oxides and titanium oxides was carried out. It was shown that an increase in the degree of defectiveness of MCNT structure ensures a more uniform distribution of metal oxides over their surface. Using quantum mechanical calculations, it is shown that improved interphase adhesion in composites may be a consequence of the chemical interaction of metal oxides with oxygen groups attached to the surface of defective carbon nanotubes. It was shown that the redistribution of electron density during the bonds formation at interphase boundaries significantly affects the electronic properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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