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Changes of the electronic structure of the atoms of nitrogen in nitrogen-doped multiwalled carbon nanotubes under the influence of pulsed ion radiation

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ABSTRACT

With the use of X-ray photoelectron spectroscopy (XPS) there have been investigated the changes of the chemical state of nitrogen atoms in the structure of nitrogen-doped multiwalled carbon nanotubes (CN_x-MWCNTs) resulting from the impact of pulsed ion beam at various parameters of the beam (energy density, number of pulses). It has been established that irradiation with the pulsed ion beam leads to a reduction of the total amount of nitrogen in CN_x nanotubes. It has been shown that a single pulse irradiation of ion beam at the energy densities of 0.5, 1, 1.5 J/cm^2 leads to restructuring of the nitrogen from pyridinic and pyrrolic configuration to graphitic state. Complete removal of nitrogen (pyridinic, pyrrolic, graphitic) embedded in the structure of the walls of CN_x nanotubes occurs at ten pulses and 1.5 J/cm^2.

1. Introduction

Currently, carbon nanotubes (CNTs) are the subject of intense research due to their unique electronic structure, electrical and mechanical properties. CNTs are used as a promising material for micro- and nanoelectronic devices [1], the anode material for lithium-ion batteries [2]. In this regard, directional change of various properties of CNTs, in particular electrical ones, is an urgent task. Doping of CNTs with nitrogen atoms [3,4] is one of the ways to operate their electrical properties. It is known that nitrogen in N-doped multiwalled carbon nanotubes (CN_x-MWCNTs) is in a variety of configurations, such as graphitic, pyridinic, pyrrolic, as well as in the form of groups NO and molecular N_2 [2,5–7]. Quantitative nitrogen content in these chemical states has different effects on the electronic structure CN_x-MWCNTs. It is possible to change directionally the chemical state of nitrogen atoms in CN_x nanotubes, for example, via controlling growth parameters using different variations of the process CVD [8–10], as well as using post-synthesis processing (annealing in air [11]/in inert environment [11,12], in acids [11,13], ozonation [14]). Wide possibilities for modifying the properties of MWCNTs arise when using a pulsed ion beam of high power density [15]. Because of appending of a large amount of power (>10^7 W) for the pulse duration (~80 ns) high pressure and temperature gradients appear, which can change morphology and affect the electronic structure of the material. By the nature of the impact this type of irradiation is close to the pulse laser irradiation. However, there are some differences, as follows: using laser impact partial reflection occurs, the value of which depends on the type of the material (metal, dielectric, semiconductor), the morphology of its surface (smooth or rough) and the wavelength of light. In the case of using pulsed ion irradiation there are almost no losses of energy for reflection. Additionally, passage of the ions in the material practically doesn't depend on the condition of the surface (morphology). In the works [16–18] it's shown that the pulsed laser irradiation of the MWCNTs films can forward the removal of amorphous carbon from the surface of nanotubes and decrease of their average diameter. Authors Li et al. in the work [19] showed that post-treatment irradiation of MWCNTs using KrF laser can significantly improve the field emission properties of nanotubes. Also, there are several works about the effect of pulsed laser irradiation on the electronic structure of MWCNTs, and there is practically no information about the impact of this irradiation on the electronic structure of CN_x-MWCNTs. To date, the information about the impact of pulsed ion irradiation

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on the chemical state of nitrogen atoms in CN_x-MWCNTs is completely missing in literature.

One of the most successful methods of the analysis of the surface which may be applicable for the study of the functionality of nitrogen atoms in carbon materials is the XPS method. This is a non-destructive method which provides the information about the electronic structure of the carbon matrix, as well as about the chemical state of impurity atoms in the surface of CN_x-MWCNTs.

As it was shown in our previous work [20], the use of a pulsed ion beam can significantly affect the electronic and atomic structure of MWCNTs. The main object of the present study is investigation of the change in electronic structure of atoms of nitrogen in CN_x-MWCNTs due to the impact of the pulsed ion beam at various irradiation parameters (energy density, number of pulses).

2. Material and methods

The layers of pure MWCNTs and CN_x-MWCNTs were grown via chemical vapor deposition through the pyrolysis of a mixture of toluene with ferrocene (100:2) and acetonitrile with ferrocene (100:2) respectively. The pyrolysis was performed at atmosphere pressure and temperature of 800 °C in argon flow (150 mL/min) on substrates of silicon wafers with 100-nm-thick oxide layers. Synthesis of carbon nanotubes continued for 15 min. The thickness of the layers of CN_x nanotubes was 20 ± 5 μm. The average diameter of CNTs is 15 nm, and the average wall thickness is 2 nm.

The layers of CN_x-MWCNTs were irradiated by pulsed ion beam using the TEMP-4 M accelerator [21] (15% H^+, 85% C^+, energy: 250 keV, pulse duration: 120 ns) with an energy density of 0.5, 1 and 1.5 J/cm^2. The number of irradiation ion beam pulses of one and ten was used. The projected ranges of hydrogen and carbon ions in a target MWCNTs layer with a density of 0.2 g/cm^3 [22] were estimated (using SRIM [23]) to be ~22.8 μm and ~5.6 μm, respectively.

The study of the transformation of the electronic structure of the samples was conducted using a surface-sensitive XPS technique at the Kratos Axis Ultra DLD analytical system. The photoemission spectra of the N 1s and C 1s were excited using a monochromatic Al Kα source (hυ = 1486.6 eV). The XPS spectra were collected with the hemispherical analyzer in fixed transmission mode, with a pass energy of 40 eV and a step size of 0.05 eV. Charge neutralization of the samples was achieved using the Kratos immersion lens neutralization system. The energy resolution of analyzer was set such that the Ag (3d 5/2) line was recorded with a full-width at half maximum (FWHM) of 0.5 eV. Binding energies were calibrated using the Au 4f 7/2, Ag 3d 5/2, Cu 2p 3/2 lines. The angle of collection for the photoelectrons, i.e., the angle between the direction normal to the surface of the sample and the axis of the analyzer, was 0°. The vacuum in the analytical chamber was maintained at 2×10^{-10} Torr. The nitrogen atomic concentration was determined from the ratio N/(C + N), where N and C are associated with the area of N 1s and the C 1s peak, respectively, taking into consideration of their relative sensitivities. Subtraction of the background from the peaks was carried out using the linear method. Deconvolution of the spectra performed by fitting Voigt profiles. For scaling reasons, all XPS spectra were normalized at its maximum value.

3. Results and discussion

Changes of the electronic structure of the atoms of carbon and nitrogen caused by irradiation with a pulsed ion beam with various parameters are shown in Figs. 1–3.

Fig. 1 shows C 1s spectra for reference samples (HOPG and pure MWCNTs) and CN_x-MWCNTs irradiated at various parameters of pulsed ion beam. Peak C 1s of pure MWCNTs has an asymmetrical shape and is located at same the binding energy as for highly oriented pyrolytic graphite (284.4 eV) which is associated with pure sp^2 C–C bonding (Fig. 1, curves 7 and 8). This indicating that carbon atoms are almost exclusively sp^2 hybridized in non-doped MWCNTs. The peak position for as-grown CN_x nanotubes is located at the binding energy of 284.7 eV (Fig. 1, curve 1). This energy shift is associated with the formation of covalent bonds C–N, when nitrogen is incorporated into the structure of the walls CN_x-MWCNTs [14,24]. As a result, some of the homopolar sp^2 C–C bonds are replaced by heteropolar sp^2 and sp^3 C–N bonds. A single shot of pulsed ion beam at different energy densities leads to a shift in the position of the maximum of the C 1s line toward lower binding energies (Fig. 1, curves 1, 2, 4 and 6). It can be noted that line-shape do not change apparently, except for a slight broadening. The greatest changes in the electronic structure of the core level of carbon in the CN_x-MWCNTs are observed upon irradiation of ion beam with an energy density 1 J/cm^2. Carbon peak is shifted to the binding energy of 284.5 eV. Shift of the line C 1s, apparently is associated with graphitization of the structure of nanotube walls, which leads to the destruction of heteropolar C–N bonds in the structure of the walls of CN_x-MWCNTs and to their replacement by homopolar sp^2 C–C bonds. Such an effect of the shift of the line C 1s to low binding energies while decreasing of the concentration of nitrogen atoms as a result of heat treatment and pulsed laser annealing of the CN_x films is convincingly demonstrated in [25,26].

Estimated values of the temperature of heating the surface of CN_x-MWCNTs layers with the pulsed ion impacts were obtained according to the data of the work [16]. It was shown that at the irradiation of the MWCNTs films with a pulsed laser (Nd:YAG) with energy density from 0.5 to 1.5 J/cm^2 there occurs the heating of the surface layer ~1 μm thick from 800 to 2081 °C, respectively. Thus, it can be said that even at the minimum energy density of the pulsed ion beam (0.5 J/cm^2) used in present work the temperature in the surface region of the layers of CN_x-MWCNTs can reach 800–900 °C. But, as it was shown above, the energy absorbed by the material at the use of the ion beam is more than for the laser. Therefore the maximum temperature in the surface layer of CN_x-MWCNTs conditioned by the impact of the pulsed ion beam

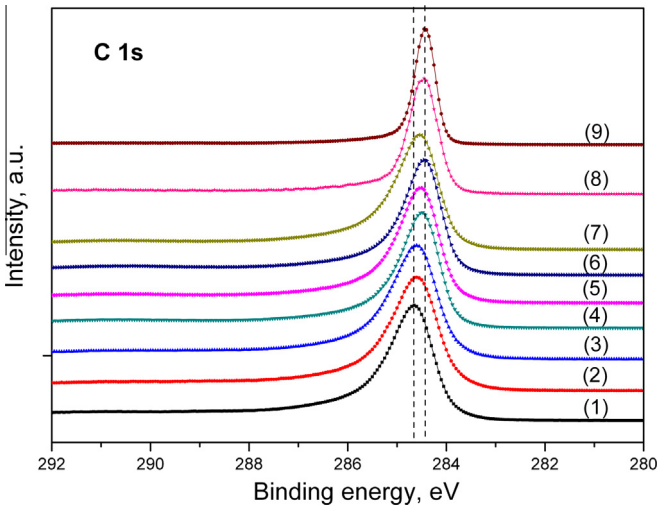

Fig. 1. Normalized C 1s core level spectra of irradiated CN_x-MWCNTs at various pulsed ion beam parameters: (1) as-grown, (2) 0.5 J/cm^2 at single pulse, (3) 0.5 J/cm^2 at ten pulses, (4) 1 J/cm^2 at single pulse, (5) 1 J/cm^2 at ten pulses, (6) 1.5 J/cm^2 at single pulse, (7) 1.5 J/cm^2 at ten pulses, (8) pure MWCNTs, (9) HOPG.