Chapter 12
Electronic Properties of Defects in Carbon Nanotubes

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Defects and their influence for electrical properties were studied in the work. It is known that defects in carbon nanomaterials, in particular nanotubes, can be formed in the process of synthesis or under external influence. And they lead to a distortion of the structure of carbon nanotubes (CNT) and the differences in properties; curved, colloidal, snakelike CNTs, tubes of variable diameters, are formed only in the presence of topological defects associated with re-hybridization and unsaturated bonds [1].

The most common distortion of the framework structure is the presence of five- or seven-membered cycles in the walls of the CNT instead of the six-membered (Stone-Wales defect), a double vacancy defect (2 V), an ad-dimer defect [2, 3]. Other class of defects is manifested in the emergence of vacancies, substitutions of carbon atoms, dislocations, and others. They can be pointy and longer. Dislocations arise in the formation of structures such as roll or papier-mache and the change the number of layers of cylindrical CNT [4]. Defects are also considered carbon atoms, which are joined by a functional group. Topological defects can disappear when heated to a temperature of up to 2773 K and higher in an inert medium.

In nanostructural materials (peculiarity of an atomic structure), each element of a system or nanocomposite has a local structure of free volume, which leads to the appearance of potential barriers limiting the movement of charge carriers at the boundary.

Positrons were used for the study of such materials [4–6], which, under the action of the electric field of the ion skeletons, migrate into a free atomic volume, where they are annihilated with electrons and give information about the electronic structure. The electronic structure depends on the conditions at the boundary of the section (height and width of the potential barriers) and the sizes of the nanostructured

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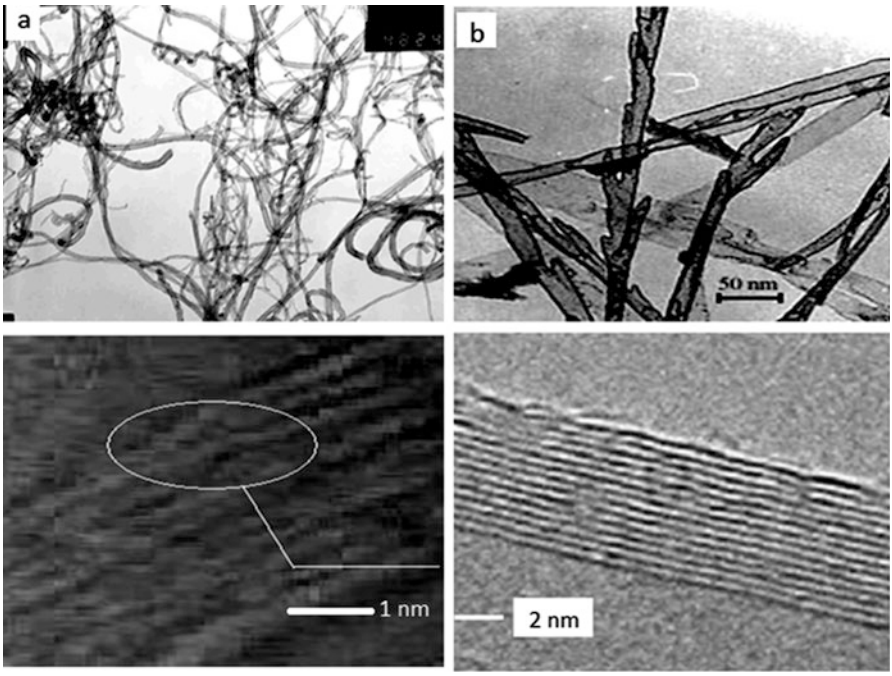

Fig. 12.1 TEM images of the CNT (**a**) with defects and boundary dislocation in CNT, (**b**) non-defect CNT and its wall

elements and determines the electronic properties of such systems and the ability to transfer electric charge [7–9]. It was shown in [4] that the free volume in nanostructured materials is characterized by the radius of localization of the wave function of the electrons, correlated with the size of interzone and intermolecular gaps and defects (vacancies, nanopores, etc.). It determines the properties of nanomaterials.

It was shown in [10] that the angular distribution of annihilation photons (ADAPh) spectra of defective tubes contains the parabolic component, in addition to the two Gaussians, and the area under a wide Gaussian is equal to 1.8 and 44% for straight and curved nanotubes, which suggests that the deviation of the form of CNT from the direct due to the presence of structural defects.

The method of the angular distribution of annihilation photons has found that in multiwalled carbon nanotubes (MWCNT), obtained under certain conditions, positrons are attracted by defects, whose transverse dimension (0.5–0.6 nm) is equal to the doubled value of the interlayer distance [4].

TEM image of nanotube shows the breakdown of the cylindrical graphene layer inside the MWCNT (Fig. 12.1a), which indicates the formation of the dislocation. Their characteristic feature is the rupture of covalent bonds on the edge of the dislocation and stretching almost twice the van der Waals bonds in its core. Such structures are quasi-uniform and extend in a circle.

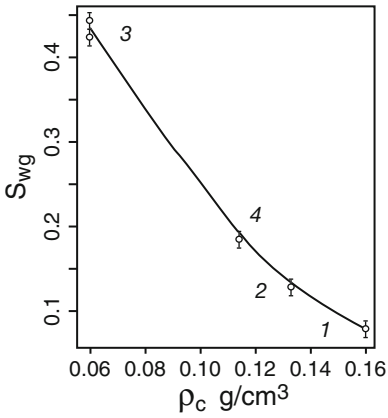

Fig. 12.2 The dependence of the area under the wide component of the ADAPh spectrum S_{wg} for CNT from the density of transition to the conductive state ρ_c. 1, 2, samples without defects; 3, sample with high concentration of dislocations; *4*, TEG

The radius of localization of the wave functions of the electrons in them is twice that of the interlayer spaces. The conditions for quantizing the energy of electrons in the nucleus of dislocations and defect-free regions are different. The interlayer distances in the nucleus of dislocations are almost twice larger than their limits, which substantially affects the positions of energy levels in the direction of dimensional quantization.

The main and excited energy levels in dislocations will be located below the positions of the corresponding levels of adjacent (defect-free) areas. This means that the electrons will be captured by the kernel of the edge dislocation. According to the electron-positron spectroscopy in nanotubes, the redistribution of electrons in the nucleus of dislocation really occurs [6]. The "capture" of free electrons in the dislocation nucleus is energy efficient. In this case, the dislocation tube can become a quasi-uniform conductor, which is locked in a circle and can form a waveguide for electrons.

Figure 12.2 shows the dependence of the area under a wide component (S_{wg}) of the ADAPh spectrum for different samples of CNT from the density of conductance state. The more defective array MWCNT has the lower density of the transition to the conductive state. Single walled carbon nanotubes - SCNT (sample 2) contains the low number of defects $S_{wg} = 7.8\%$, the transition to the conductive state is the largest $\rho_c = 0.16$ g/cm^3, and for the most defective tubes (sample 3), $S_{wg} = 42.5\%$ and $\rho_c = 0.05$ g/cm^3. This means that the most defective tubes have the most "loose" structure, in which the flow of current occurs at a lower density of the array of CNT. This is consistent with the results of work [5].

The experimental point for the TEG with a different structure compared to the nanotubes (Figs. 12.2 and 12.4) is imposed to the curve.

Properties of an array of carbon nanotubes or a material containing CNT are different from the properties of individual nanotubes. Array of CNTs doesn't conduct an electric current, in contradistinction to individual nanotubes. This is due to the fact that the connections between adjacent nanotubes are van der Waals.

It is known that in the radial (transverse) direction, nanotubes do not conduct an electric current. However, an electric current starts to pass through a CNT array when compression is under a piston, and the connection between adjacent nanotubes may even become metallic. Therefore, the measurement of the electrical properties of the CNT array was carried out under the low pressure. At the same time, the reorientation of each individual CNT, the reduction of the distances between them, the deformation of the CNT, the increase of the contact area between the nanotubes, and the reduction of the interlayer distances in the direction of the force's effect are taking place. Each nanotube has its random spatial configuration, which depends on the type and number of defects in the graphene layer and defects in the packaging of graphene layers in a nanotube (edge dislocation).

In [11], experimentally, it was shown that the bundle of oriented nanotubes under the influence of cyclic deformation retains its elastic and mechanical properties. The effect of mechanical deformation of the array of contacting nanotubes may be more complex due to the presence of contacts between adjacent nanotubes, nanotubes and metal electrodes, etc.

The features of electrical conductivity of the spatially unoriented nanotube array (sample 2) and nanotubes (sample 3) were investigated from their density σ(ρ), which varies during compression during loading and unloading in a dielectric cylinder under a piston.

These samples differ from other largest concentrations of free electrons according to EPS data [3]. The TEM image (Fig. 12.1a) shows a break in the cylindrical graphene layer inside the CNT, indicating the formation of a boundary dislocation and which is not a characteristic of defect-free CNT (Fig. 12.1b).

The statistical distribution of CNT on the outer diameter showed that it is 10–20 nm.

The dependence of the electrical conductivity of an array of bulk carbon nanotubes (sample 2) on the density of the compressed array of CNT in the direct and reverse piston movement for the first measurement cycle is given on Fig. 12.3.

In the process of lowering of the piston, the electrical conductivity is $\sim 10^{-5}$ $(\text{Ohm} \cdot \text{cm})^{-1}$ and fixed for the density $\rho_c = 0.081$ g/cm^3, and for the density $\rho = 0.11$ g/cm^3, the electrical conductivity increases up to five orders of magnitude

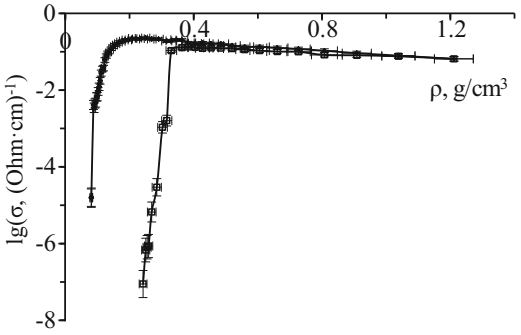

Fig. 12.3 Dependence of the logarithm of electrical conductivity lgσ of the array of multiwall carbon nanotubes without dislocations on the change in density ρ under the action of deformation and subsequent discharge. ◆, loading; □, unloading

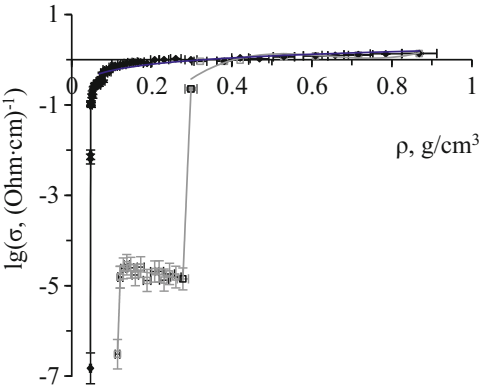

Fig. 12.4 The dependence of the logarithm of the electrical conductivity lgσ of the MWCNT array with boundary dislocations on the change in density ρ under the action of deformation and subsequent discharge. ◆, loading; □, unloading

and the value is 0.23 (Ohm cm)$^{-1}$. Further compression of the CNT to the density $\rho = 1.21$ g/cm^3 leads to a monotonous drop in electrical conductivity up to 0.065 (Ohm cm)$^{-1}$.

During discharge, the volume increases, and an elastic relaxation of the CNT array, which maintains contact between the nanotubes and the electrodes, is observed. From Fig. 12.4 it is evident that the electrical conductivity $\sigma(\rho)$ during unloading increases twice, to 0.13 (Ohm cm)$^{-1}$ in the range of densities ρ from 1.21 to 0.38 g/cm^3, after which the jump falls to six orders that were fixed at $\rho = 0.24$ g/cm^3. When further unloading, the process of elastic relaxation is completed, and there is a break in the electric circuit.

For MWCNT with dislocations, the dependence of the electrical conductivity of the bulk of CNT from their density at the forward and reverse piston stroke for the first measurement cycle is shown in Fig. 12.4. When compressing the bulk sample in the process of loading the piston, the value of the electrical conductivity, which is equal to $\sigma = 1.50 \cdot 10^{-7}$ (Ohm cm)$^{-1}$, is fixed for the density of the nanotube array $\rho_c = 0.05$ g/cm^3, and at density $\rho = 0.11$ g/cm^3, the electrical conductivity increases by 10^6 times and reaches a value equal to $\sigma = 0.71$ (Ohm cm)$^{-1}$.

Further compression of the CNT to the density $\rho = 0.86$ g/cm^3 leads to a gradual increase in electrical conductivity else 48%. From Fig. 12.4 it is evident that the electrical conductivity $\sigma(\rho)$ in the reverse sequence repeats the course of the curve at compression $\sigma(\rho)$ in the range of densities ρ from 0.86 to 0.30 g/cm^3, after which the electrical conductivity falls 10^4 times; then in the range ρ of 0.30 to 0.12 g/cm^3, there is an almost horizontal stair. With further increase in discharge, electrical conductivity drops rapidly due to a decrease in the total area of the contacts and a break in the electric circuit.

The density of the transition to the conductive state for CNT with dislocations is 0.05 g/cm^3 (Fig. 12.4), which is lower than for CNT without dislocations (0.08 g/cm^3): CNT with dislocations deviates to a greater extent from ideal rectilinear CNT. The deviation of their shape from the ideal is also confirmed by the presence of twisted regions and clusters on their TEM images (Fig. 12.1a).

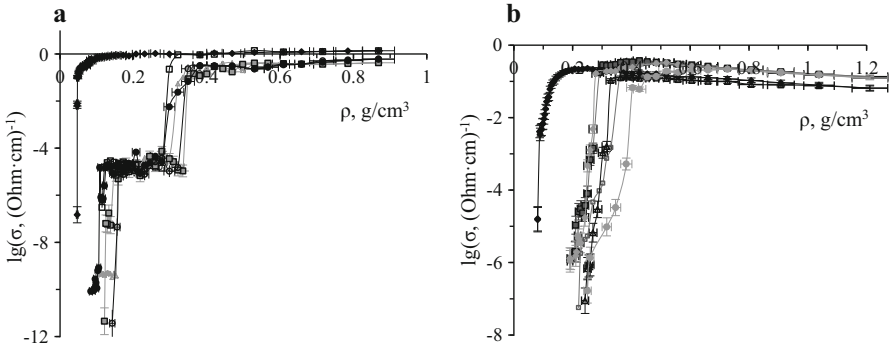

Fig. 12.5 Influence of cyclic deformations on the electrical conductivity σ(ρ) of MWCNT (**a**) with dislocations for 1, 3, and 5 measurement cycles: 1, ◆; 3, ●; 5, Δ (loading); 1, □; 3, ○; 5, ■ (unloading), (**b**) CNT without dislocations for 1, 2, and 4 measurement cycles: 1, ◆; 2, ◆; 4, ■ (loading); 1, Δ; 2, ●; 4, □ (unloading)

The array of nanotubes with boundary dislocations was exposed to loading-unloading by 12 cycles.

For the second and subsequent loading/unloading cycles for a given CNT array (Fig. 12.5a), two jumps and steps were observed both during loading and unloading, which are not observed for defect-free CNT (Fig. 12.5b).

After four cycles of deformation of the loading-unloading of the CNT without dislocations, the transition to the conducting state increases from 0.08 to 0.22 g/cm^3 (Fig. 12.5b), which is almost identical to the relaxation transition $\rho_{rel} = 0.23$ g/cm^3. This testifies to the ordering of CNTs in the process of cyclic deformation.

For CNT with dislocations, from 2nd to 12th cycles of loading-unloading, the transition to the conductive state is recorded in the density range $\rho_c = 0.06$–0.10 g/cm^3. There is a tendency to increase this value with an increase of the number of cycles, which may indicate an increase in the density of the packaging of an array of CNT and their predominant orientation. For all cycles of measurement, the stair on the density curve of the electrical conductivity has an almost constant value $\sigma = (2.4 \pm 0.3)\cdot 10^{-5}$ (Ohm cm)$^{-1}$, which is stored in the density range from $\rho = 0.12$ to 0.30 g/cm^3. The return motion of the piston for the first measurement of the electric jump is observed at $\rho = 0.30$ g/cm^3, and its incidence is four orders of magnitude. For the next cycles, the density at which the jump σ is observed increases to 0.38 g/cm^3. The second jump in the reverse direction of measurements for the first measurement is observed at $\rho = 0.12$–0.28 g/cm^3 and for subsequent cycles of measurements increases to $\rho = 0.30$ g/cm^3.

The first jump of electrical conductivity is due to the transition of dielectric state to the metallic, the second one is due to the change in the mechanisms of electron transport, and the step that connects them is due to the elastic properties of twisted bundles without deformation.

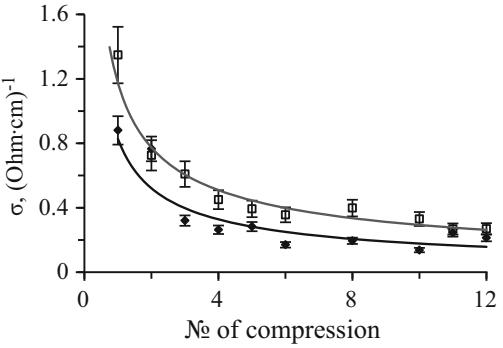

Fig. 12.6 Processes of the ordering of the CNT array under the action of cyclic loading-unloading processes. ◆, compression density $\rho = 0.50$ g/cm^3; □, $\rho = 0.86$ g/cm^3

The effect of the number of loading-unloading cycles for the electrical conductivity for compression to density $\rho = 0.86$ g/cm^3 (maximum compression) and the value of electrical conductivity for density $\rho = 0.50$ g/cm^3 is shown in Fig. 12.6.

It is evident that the electric conductivity falls to the fifth to sixth cycle, after which it remains practically unchanged, which indicates the ordering of the CNT array under the action of cyclic loading and unloading.

12.1 Conclusion

The more defective array MWCNT has the lower density of the transition to the conductive state. This means that the most defective tubes have the most "loose" structure, in which the flow of current occurs at a lower density of the array of CNT.

During cyclic deformation CNT array containing edge dislocations, nanotubes are targeted and ordering, and on the dependence of conductivity of array density, there is a two-stage jumping conductivity by several orders, combined stair. They are caused by the action of three mechanisms:

1. Increasing number of contacts and their total area
2. Elastic deformation swirled into a spiral or circle (radius of 100–1000 nm) nanotubes
3. The changing nature of electron transfer at points of tangency of the tunnel to the semiconductor and metal

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