Interpretation of dynamic and dc field-emission characteristics of nanocarbons in terms of two-stage emission model

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Different nanostructured carbons demonstrate notable electron emission in low-magnitude electric field. In the case of nanotubes and fibers, this feature is associated with field focusing at sharp tips. For other materials, with relatively smooth surface morphology, the actual mechanism of emission enhancement remains unclear. Being different in many aspects, most efficient emitters of this type do have common features: 1) their surface layer is heterogeneous, includes both sp^2 and sp^3 grains and/or numerous structural defects. 2) work function values derived from emission I-V plots in accordance with Fowler-Nordheim (FN) formula (0..1.5 eV) prove to be much lower than ones determined with other methods (optical or thermionic emission) and than values generally typical for carbon (>4 eV). Different authors consider field-induced emission from such materials as a two-stage process involving transient acceptor-type states in the surface layer – for instance, conduction band states of a diamond-like film or grain. Now, we apply this two-stage model to the results of experimental study on emission from nanocarbons in non-stationary (pulsed) field [1,2]. Both digital and analytical modeling confirmed that the emission hysteresis observed in the experiments can be explained via dynamics of electron population at transient states. To simulate modification of I-V plots with variation of field pulse parameters (amplitude, dc bias, pulse shape and length) and with emitter activation/degradation, the coulomb field of electrons at the surface states had to be put into account.

The developed model allowed us to associate parameters of dynamic and static I-V plots with emission centers' properties. For a sufficiently short field pulse, when the surface charging effect is negligible, the direct (measured at the field increase) I-V plot branch follows the FN law with the slope determined by the material work function. The inverse branch has much lower slope determined by the peak field achieved earlier in the pulse. In static regime (dc or long pulse) both branches coincide, and their inclination to the axis in FN coordinates gives us the value of surface electron affinity (conduction band bottom energy – for emission via a diamond like phase inclusion). In our experiments, the static and the dynamic direct branch slopes' ratio was about 1:3, which corresponds to sensible values of 4.5 eV for work function and ~3 eV for the transient layer material band gap.

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On possible structure of field-induced electron emission centers of nano-porous carbon

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Nano-porous carbon (NPC) gives a good example of carbonic material with "smooth" surface morphology demonstrating promising field-emitter properties [1]. Electron current extracted from NPC exceed predictions of classic Fowler-Nordheim theory by a few orders of magnitude. For many other micro- and nano-structured carbons, this feature is explained by interaction between domains with sp^2 and sp^3 hybridization of C atoms. In this model, graphite-type areas secure electron transport to the sample surface, where electrons tunnel onto conduction-band states of a diamond-like film, grain or inclusion separated from vacuum by only a thin and low barrier. This process is possible due to low conductivity of sp^3 carbon, which allows electric field to penetrate into its volume to reduce energy of the conduction band bottom below volumetric Fermi level. We propose modification of the model to make it relevant to the case of fully graphitic NPC.

According to [2], NPC is a porous conglomerate of small (1-2 nm) graphene sheets mixed with larger onion-like particles (up to 50 nm in size). Electrophysical properties of the material are those of a p-type semiconductor, which means non-zero bandgap and Fermi level position below the top of the valence band. The excessive holes appear due to trapping of electrons at interface boundary states, thus all crystalline volumes are charged positively relative to their boundaries. Due to strong band bending effect, grains are separated by tunnel junctions. In this situation, a grain of optimal size and conductivity situated at the surface can efficiently emit electrons. Its polarization in external field leads to field enhancement at the junction separating it from the rest of the sample. If this junction switches to tunnel-diode regime, electrons from the Fermi level are injected to the conduction band of the surface grain, which facilitates their further transfer to vacuum. Viability of this scenario for NPC is confirmed with quantitative estimates and simulation.

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"Fine structure" of emission I-V characteristics of nano-dispersed films

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Current characteristics of field-induced emission from nano-structured films are assumed to follow exponential dependency (or, more precisely, Fowler-Nordheim (FN) formula), as do characteristics of metallic tip emitters. Yet, the general exponential trend is usually derived from experimental data sets having substantial irregular component, associated with instability of emission properties of film emitters. Besides noise-like fluctuations, experimental curves often include instant drops of current, sometimes by as much as an order of value or more. Observation of emission images (area distributions of current) shows that some centers of active emission can be simply "turned off" at certain moments. It is natural to consider such an event as a case of destruction or de-activation of this center. However, in experiments with nano-porous carbons and other promising emitter films we discovered these current drops to be reproducible (repeating in a series of measurements) and reversible (reducing-field plot branch shows current rise at approximately the same field value).

This phenomenon of reversible de-activation of emission sites can be explained by the two-stage emission model with participation of acceptor-type transient electron states localized in a surface layer. Penetration of external electric field into emitter reduces the energy of the surface states. Electron current to the transient states (and then to vacuum) starts as this energy reaches Fermi level. Yet, with further field increase, continued downshift of surface states' energy can result in their insulation from emitter volume, which leads to interruption of emission current. "Fine structure" of emission I-V plots may be useful for reconstruction of electronic properties of emission centers (that is still unclear for many promising emitter materials). Also, current limitation can represent an advantageous property for distributed emitter systems, allowing to avoid destruction of emission sites by excessive current and to achieve more uniform emission distribution.

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Facilitating effect of non-stationary electric field on electron emission from nanocarbon films

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Previous experiments have demonstrated that non-stationary electric field can have temporary enhancing effect on field-induced electron emission from a few types of nanostructured carbons comprised by low-aspect-ratio particles [1,2]. This effect finds no direct explanation in Fowler-Nordheim theory, but fits well in the model of emission via acceptor-type transient states localized in the surface layer of the nanostructure, where electron states' energies are influenced by the external field. Recently performed computer simulations showed good agreement with experimental characteristics, provided that the model system includes two sets of surface transient states with different parameters and different (but close) localization. The deeper states are filled with electrons as soon as electric field is turned on, but the potential barrier separating them from vacuum is too high to allow efficient emission. The shallower states, having good connection with vacuum, remain empty in static or slowly changing field, as their energy doesn't reduce below the Fermi level. Introduction of a short field kick pulse results in charge exchanged between the sets of transient states, and the shallower states are populated with electrons, which boosts emission current. This scenario looks generally realistic, because in the presence of non-stationary field the whole system becomes non-conservative, and some part of electrons can acquire additional energy facilitating their emission. Further simulations demonstrated that under the effect of rf field component of sufficient magnitude, the activation of emission properties remains permanent. The necessary rf field magnitude can be reduced for a system with larger number of interacting states, serving for consecutive elevation of electron energy in a series of inter-state transitions.

Even in the case of static external electric field, electron energy distributions can be distorted by non-conservative field effects – the ones associated with auto-oscillations of emission current, experimentally observed in our previous work [3]. In the digital model, such oscillations developed in systems with one or two transient states. The oscillatory mechanism required a start-up excitation, but then its magnitude was self-maintained and supported huge increase of emission current.

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Research of dependence of SWCNTs dipole moment on its length

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For the purpose of studying possibility of use carbon nanotubes [1] as gauges research of dependence of SWCNT's dipole moment on their length has been carried out. In this work the polarized carbon nanotubes of two structure modifications: (n, n) and (n, 0) are used as a research object. Boundary broken bonds are isolated on one side by hydrogen atoms and on another by fluorine atoms. The length of tubes has been varied.

To determine the mentioned above dependence the electronic structure and the power characteristics were calculated with use of semi-empirical methods of quantum chemistry [2]. The dependence of the dipole moment on the number of elementary cells along nanotube's axis is computed. The obtained data show, that dependence of the nanotube's dipole moment on the length has a nonlinear character. It makes possible the application of carbon nanotubes as the sensor controls reacting even on weak electromagnetic signals. Dependences of charges on boundary atoms of fluorine and hydrogen have a similar character.

These values have some oscillations. We can see it in even and odd lengths (elementary cells). In tubes (n, 0) does we have not same results.

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Electrical field amplification in electron field emitters on the basis of carbon nanotubes

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The problem of evaluation of the electrical field amplification factor in electron field emitters on the basis of carbon nanotubes (CNT) has been analyzed. There has been stated and resolved the electrostatic problem for determination of the electrical field amplification factor for CNTs with different tip structure, depending on the tilting angle of a CNT relating to the cathode plane and the inter-electrode spacing. There has been calculated the dependence of the electrical field amplification factor for an array of vertically aligned CNT on the spacing between the nanotubes. This dependence has been used for evaluation of the optimum surface density of CNTs in the array, providing the maximum magnitude of the emission current density. The current-voltage characteristic of a CNT-based cathode with taking account the statistical spread in the tilting angle has been calculated. This characteristic is compared with that obtained earlier with taking account the statistical spread of geometrical parameters of CNTs.

High current density planar field electron emitters with carbon nanotubes

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Planar field electron emitters with carbon nanotubes are very promising for usage in various electron devices. However only emitters characterized by high emission current density (about 1A/cm^2) are suitable for usage in powerful microwave devices. If the emission current density is so high, strong heating of nanotubes takes place, that at the presence of electrostatic forces can cause the shortening of separate nanotubes, or even the tearing them off the substrate. Namely this effect apparently causes the degradation of planar field electron emitters with carbon nanotubes at high current density, that has been described in literature. The present work is devoted to the investigation of the change of the concentration of the emitting carbon nanotubes in planar field electron emitters under the passage of high emission current.

We have developed planar field emitters with carbon nanotubes that possessed stable emission at high current densities about 1A/cm^2. Field emitters have been manufactured by CVD method and consisted of nonoriented nanotubes 10-50 nm in diameter and about 10 μm long. The analisys of current-voltage characteristics of such emitters based on Fowler-Nordheim theory allowed us to calculate not only the field amplification coefficient β, but also the emitting area A, and to estimate the number of emitting nanotubes N before and after high emission current passage, i.e to estimate the change of the amount of emitting nanotubes at the high current passage. We have found that the concentration of the emitting nanotubes in such field emitters after the passage of high emission current was about 10^5 cm^2.

Also in the work the location of light, radiated by nanotubes heated by high emission current ($j \geq 100$mA/cm^2) have been investigated. This effect has given possibility to localize regions of the emitter surface that gave the main contribution to the electron emission.

Study of bismuth nanoparticles and nanotubes obtained by microwave heating

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Microwave synthesis of bismuth nanotubes, as an easier and less expensive method to produce Bi nanotubes, is reported. The nanotubes were prepared by heating Bi powder in vacuum during 5, 10 and 15 minutes in a conventional microwave oven of 2.45 GHz and 800 W. The resulting Bi nanotubes were characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). Computer simulation software was used to predict stable configurations for a (6,6) Bi nanotube to study the ground energy state and electronic properties of this configuration.

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Fe-filled carbon nanotubes produced by microwave heating of ferrocene

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Highly efficient one-step microwave technique (MW) was applied to obtain long and aligned carbon nanotubes with or without Fe filling. Carbon nanotubes (CNTs) were produced by microwave irradiation heating from a ferrocene $Fe(C_5H_5)_2$ as a precursor. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) were used to study the growth process of aligned carbon nanotubes during microwave heating. Formed CNTs have a metal particle at the tip of each tube. This carbon nanostructure promises attractive for nanoscale engineering of fuel cells and other systems.

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The pulse discharge method for carbon nanotube ring production

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Carbon nanotubes rings (CNR) – is a new form of nanostructured carbon. It possesses unique electro-magnetic, mechanical and chemical properties. CNR have great perspectives in nonvolatile memory and materials with high mechanical properties. So it's very important to have stable and high-performance method of CNR production.

We have developed the CNR growth system to produce nanorings with predicted electromagnetic characteristic and shape. [1]

The system consists of horizontal cylindrical reactor with electronic controller, plasma source, forepump and evaporating chamber, which supply carbon-bearing gas-vapor mixture (CGM). Vacuum, gas flow rate and discharge parameters are precisely set by controller. The growth camera is made of heatproof metal with anticorrosive properties. We have realized two deferent methods of CGM supply: barbotage through carbon-bearing liquid by ambient air or alcohol evaporation with temperature control.

In this work we used 2-propanol as carbon-bearing liquid. The process of nanorings growth consists of several stages. At the first stage of CNR growth process the nanoclusters of catalytic metal (alloy of Fe 60-70%, Ni 10-15%, Cr 15-20%) are produced from cathode (by spark erosion machining) in vacuum. After that the gas is pumped into the reactor increasing the number of alcohol molecules in interelectrode gap. At the next stage the spark discharge evolve in shot-time arc discharge providing the growth of nanotubes vortex magnetic field, which induce nanotubes to form rings.

At the end of process we must separate CNR from the amorphous carbon and other nanotubes. The nanomaterials was dispersed in isopropyl alcohol with making use of ultrasonic bath. We suggest that nanorings can be separated by magnetic field because amorphous carbon and nanotubes (unlike carbon nanorings) are not magnetic materials.

The material produced in the experiments were investigated using atomic-force microscope (AFM). It was shown that received carbon nanotubes rings have 1-5 nm in diameter of tube and 100 nm in ring diameter.

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Studies on electrochemical properties of aligned multi-walled carbon nanotube electrodes

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Aligned multi-walled carbon nanotubes (MWNT) have been the subject of intense research for applications in modern technologies. We have investigated electrochemical properties of electrodes with aligned MWNT synthesized using chemical vapor deposition on Ti, TiN, Ni, Nb substrates with with ferrocene as catalyst precursor and xylene and H_2/Ar mixture as carbon source and carrier gas respectively [1].

Structure and morphology of aligned MWNT electrodes have been carred out using scanning electron microscopy. The average tube diameter is around 35 nm. The depth of the tube layer is from a few microns to several dozen microns, depending on deposition time and type of metal.

The electrochemical properties of the aligned MWNT electrodes were investigated by cyclic voltammetry (CV) in the standard three-electrode cell. The CV results showed that aligned MWNT electrodes could be of great significance in both fundamental and applied electrochemistry.

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Influence of CVD parameters on growth of aligned carbon nanotube arrays

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Chemical vapor deposition (CVD) is a method allowing modifying the structure and composition of carbon nanotubes (CNTs) with tuning parameters. Temperature, reaction mixture engagement rate, concentration of the catalyst, reaction mixture composition, pressure, gas flow rate, and synthesis duration are very important for CNT synthesis. If even one parameter is varied the properties of all system, and, hence, and properties of investigated objects will be changed. In the present research we study effect of modification of reaction mixture with adding of nitrogen-containing component on the structure and composition of CNTs. It is known that decomposition of nitrogen-containing compounds results in nitrogen doping of CNTs but relationship between proportion of nitrogen and carbon atoms in the reaction mixture and the doping level of CNTs is still poor understood. The other variable parameter of CVD process was the time of injection of the reaction mixture in a zone of growth of aligned CNT array. We expected to determine the rate of CNT growth. All experiments have been done at temperature 800°C and carrier gas flow of 150 ml/minute at atmospheric pressure. Acetonitrile was used as a nitrogen source. The second reaction mixture component was toluene. Thus, the solution of acetonitrile in toluene with concentration varied from 0% up to 100% and with 25% step was tested. Transmission electron microscopy showed that incorporation nitrogen in CNT walls leads to formation of bamboo-like structure or to corrugation of walls. Concentration of nitrogen in CNTs was determined from CHN-analysis. To check how duration of CVD process influences the thickness of CNT array formed on silicon support the synthesis was made one, two, and three hours. At one hour duration, the dense black film having 0,5 mm thickness was formed on the substrate. Increase of synthesis time up to two and three hours contributed to respectively 1 mm and 1.5 mm thickness of CNT film.

Comparative X-ray investigation of fluorinated single- and few-wall carbon nanotubes

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Fluorination is very attractive for covalent functionalization of carbon nanotubes (CNTs) because of possibility to attach a large amount of foreign atoms to the CNT surface without destruction of the tubular morphology. The goal of the present work is to investigate the reactivity of different types of carbon nanotubes (CNTs) toward fluorination and influence of Ar^+ ion irradiation on the structure of fluorinated CNTs.

The single- and few- wall carbon nanotubes (SWCNT and FWCNT) were synthesized by catalytic chemical vapour deposition method. Additionally, we examined the samples, which were milled using the ball milling apparatus (Pulverisette 0, Fritsch). Transmission electron microscopy investigation showed the SWCNTs sample contains single-wall CNTs (63%) and double-wall CNTs (31%). The FWCNTs sample contained double-wall CNTs (29%), triple-wall CNTs (54%) and four-wall (9%) nanotubes. Pristine and ball-milled samples have been fluorinated at room temperature using gaseous BrF_3 as a fluorinating agent. The X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) experiments were performed at the Berliner Elektronenspeicherring fьr Synchrotronstrahlung (BESSY) using radiation from the Russian-German beamline. Ar^+ ion irradiation of CNTs was performed in vacuum chamber of the spectrometer. The C 1s XPS and C K-edge and F K-edge NEXAFS spectra were used to estimate the chemical composition and to probe the electronic structure of the fluorinated CNTs. Analysis of the XPS C 1s spectra showed that relative to the SWCNT samples, the FWCNT samples incorporate less fluorine quantity because the inner shells remain intact. The ball-milling of the samples during 1 hour has insignificant effect on CNT length and more likely produces defects in CNT surface layers. These defects increase fluorination ability of CNTs and provide access for fluorine atoms to the subsurface layers of FWCNTs. Ion irradiation of pristine and fluorinated CNTs created structural defects in CNTs. F K-edge NEXAFS spectra of the fluorinated CNTs after ion irradiation showed residual amount of fluorine atoms in sample.

Piezoresistance effect in carbon nanotubes

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The piezoresistance effect is in the change of the electroconductivity of the semi-conductors caused by the anisotropic deformation of a crystal [1]. The piezoresistance effect in single walled carbon nanotubes [2] of two geometry modifications "arm-chair" and "zig-zag" has been investigated. The electronic structure of nanotubes has been simulated within the framework of π-electronic approach and Hubbard's model [3] taking into account only for the energy of electrons in carbon atoms and the energy of the transition between the neighbor lattice units. The band structure of carbon nanotubes is described by the dispersion relation for the graphite sheet [2]:

$$\varepsilon(k_x, k_y) = \pm\gamma_o \left\{ 1 + 4\cos\left(\frac{\sqrt{3}k_x R}{2}\right)\cos\left(\frac{k_y R}{2}\right) + 4\cos^2\left(\frac{k_y R}{2}\right) \right\}^{1/2}, \quad (1)$$

where γ_0 is the transfer integral, k_x and k_y are the wave vector components, one of which is continuous along the tube axis and another is quantized along the tube circumference according to "arm-chair" or "zig-zag" geometry type, R is the interatomic distance, which has been defined to be equal 1.44 Å.

The bulk and linear deformations have been simulated by small changes of the bond length R. The band structure change caused by small deformation can be expressed within the framework of the linear approximation as following:

$$\varepsilon(k_x, k_y) \approx \varepsilon_0(k_x, k_y) + R\frac{\partial\varepsilon}{\partial R}\delta, \quad (2)$$

where $\varepsilon_0(k_x, k_y)$ is the band structure of a non-deformed carbon nanotube (1), δ is the relative change of the carbon-carbon bond length.

The band structure changes, which influence on conducting properties of carbon nanotube and cause the piezoresistance effect, have been analyzed. The effect can be used for the identification of single walled carbon nanotubes and the development of electro-mechanical energy transformers.

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Influence of point defects on band structure of carbon nanotubes within the framework of the periodical Anderson's model

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The theoretical researches of the physical properties of single walled carbon nanotubes [1] remain the actual problem of modern physics of the nanostructures. This work is devoted to the analysis of a band structure of carbon nanotubes with the point defects in a crystal lattice.

As carbon nanotubes have the conjugated chemical bonds it is expedient to use the π-electronic Huckel's approach and the periodic Anderson's model [2]. This model considers two groups electrons: collective and localized. The interaction between two kinds of electrons is realized by the hybridization potential. The collective electrons are considered as free but the localized electrons are coupling by means of the Coulomb interaction on the same unit. The periodic Anderson's model is described by the following Hamiltonian:

$$H = \sum_{k\sigma} \varepsilon_k a^+_{k\sigma} a_{k\sigma} + \sum_{a\sigma} \varepsilon_a d^+_{a\sigma} d_{a\sigma} + \sum_{ak\sigma} V_{ka} (a^+_{k\sigma} d_{a\sigma} + d^+_{a\sigma} a_{k\sigma}), \qquad (1)$$

where $a^+_{k\sigma}, a_{k\sigma}$ are the Fermi operators of the creation and the annihilation of electrons with the wave vector $\boldsymbol{k}$ and the spin σ, $d^+_{a\sigma}, d_{a\sigma}$ are Fermi operators of the creation and the annihilation of electrons of the impurity, ε_k is the band structure of the ideal nanotubes, ε_a is the electrons energy on the defect, V_{ka} is the Fourier image of the hybridization energy. The parameters ε_a and V_{ka} of the Anderson's Hamiltonian were calculated by the quantum-chemical semi-empirical method MNDO [3].

Within the frameworks of the Green function method the energy dispersion relations of carbon nanotubes with the point defect is described by the formula:

$$E(k) = \frac{1}{2}\left[\varepsilon_a + \varepsilon_k \pm \sqrt{(\varepsilon_a - \varepsilon_k)^2 + 4|V_{ka}|^2} \right], \qquad (2)$$

In this work the change of the band structure of carbon nanotubes caused by single defect was analyzed and the influence of the defect concentration on the zone structure has been investigated also.

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The effect of different treatments on electrical resistivity of carbon nanotubes

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During the last two decades carbon nanotubes (CNT) began to play a significant role in different nanotechnologies. With the decrease of CNT's cost the demands for nanotubes are increasing rapidly for mechanical, medical and electrical applications.

Many different companies produce a great number of CNT and also they give more or less determinated properties of products. But in reality we have to check conductivity, mechanical or thermal properties of initial CNT for every case of their utilisations.

The differences and uncertainties of CNT properties result from not only different methods of testing, but also due to both the legend of their production and their temporary instability.

The aim of our work was to understand how the electrical conductivity of multi-walled carbon nanotubes (MWCNT), used in the experiments, can be changed by thermal treatment under the inert atmosphere or by oxidation.

It was determined that the electrical resistivity of MWCNT decrease with increasing of temperature and increase during the following exposition on air. The difference between electrical resistivity of MWCNT before and after thermal treatment may be in 3 times.

As a consequence the electrical resistivity of polymer composite materials filled by thermally treated MWCNT is also decrease.

Based on data of X-Ray photoelectron spectroscopy we suppose that the change of electrical resistivity can be explained by oxidation or reduction of the surface of CNT.

Spin-triplet molecule inside carbon nanotube

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Recently the behaviour of a molecule, placed within fullerene or carbon nanotube, has attracted theoretical [1] and experimental [2] interest. Control of rotation of such endohedral system may be used in molecular electronics. Besides, quantum mechanics itself gets novel problems to solve, e.g. the coupling of molecular rotation and exchange interaction. Being chemically isolated, endohedral molecule may carry a lone electron pair [3-5], whose exchange interaction with the nanotube electrons contributes to the Hamiltonian [6]:

$$H=a\,\boldsymbol{L}^2+(\mu\,H_0+b\,n_z)S_z+c(n_x\,S_x+n_y\,S_y)$$

Energy constants refer to spherical top rotation (a), and exchange interaction (b, c) depending on molecule distance from the nanotube wall. The simplest model is considered, where integer angular momentum $\boldsymbol{L}$ of entire molecule acts on its principal-axis ort $\boldsymbol{n}$, spin operator $\boldsymbol{S}$ acts on lone electron pair with magneton μ. Magnetic field $\boldsymbol{H}_0$ is aligned with the nanotube axis. The conservation of the total moment's $\boldsymbol{J}=\boldsymbol{L}+\boldsymbol{S}$ axial z-projection allows one to develop *eigen*functions over spherical harmonics $Y_{L,M}(\boldsymbol{n})$, and 3-component spinor orts $\Gamma_{1,S}$, e.g.

$$\langle\boldsymbol{n}|N,\,J_z=0\rangle = \Gamma_{1,0}Y_{0,0}A_0+\Sigma_{L>0}\{\Gamma_{1,0}Y_{L,0}A_L+\Gamma_{1,+1}Y_{L,-1}B_L+\Gamma_{1,-1}Y_{L,+1}C_L\}$$

Principal quantum number N=1, 2,... orders energies and numerates *eigen*vectors $\{A_L,\ B_L,\ C_L\}$. We have received matrix secular equations (of infinite order) in analytic form, and then by means of a numerical method have found their approximate solutions with the lowest energies.

The results may be applied to the EPR experiments with the nanotube-encapsulated spin-triplet molecules like $H_5C{-}C^*{=}C{=}C^*{-}CH_5$, whose lone-pair electrons are localized as noted in chemical formula [4]. Consider a novel effect, predicted by our calculations: abrupt switching of magnetic field will change a rotational state of the molecule. Another control technique may use an electric current pulse through the nanotube.

Grant-in-aid 08-03-97000 from Rus. Basic Res. Foundation is acknowledged.

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The influence of adsorbed molecular hydrogen on band structure of carbon nanotubes

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The big number of papers, both theoretical, and experimental recently is devoted to hydrogen adsorptions on a carbon nanotube (CNT) [1] surface. The exhaustion of energy resources and environmental contamination are actual problems which demand the immediate decision. Molecular and atomic hydrogen adsorption on CNT surface have been investigated in the paper. The methods of the statistical physics, mathematical device of the Green Functions for solution problem were used.

In the work the results of theoretical quantum statistical research of atomic and molecular hydrogen adsorption on a surface single-wall carbon nanotubes within the framework of Anderson's model [2] are presented. The band structure of adsorption systems are calculated as follow:

$$E(k) = 0.5\left(\varepsilon_a + \varepsilon_k \pm \sqrt{(\varepsilon_a - \varepsilon_k)^2 + 4\left|V_{ka}\right|^2} \right) \qquad (1)$$

Change of a zone as a result of atomic adsorption is analysed. It is predicted, that binding of single hydrogen atom decrease the band gap of semiconducting carbon nanotubes. Qualitative change of a zone is observed also in area of an adatom level (approximately -10 eV), located in depth of a valence band. In this area there are additional zones owing to interaction of hydrogen atom with a valence band. At plural adsorption there is a change of population levels, and for sufficient adatom's energy levels can cross Fermi's level, for example alkaline metals. For atoms of hydrogen there is only a displacement of a valence band upwards.

The constructed model has been used for the analysis of change of carbon nanotubes physical properties as a result of monovalent atoms adsorption. In the constructed model the Coulomb electrons correlations are not considered.

For molecular adsorption Coulomb electron correlations of defect are considered.

This work was supported by grant RFFI (№ 08-02-00663).

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Physically-mechanical properties of poly(vinyl) chloride with multi-walled cardon nanotubes

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Multi-walled carbon nanotubes are generally used for production of polymer composites whereas they have high elastic properties and durability parameters. Such characteristics have only nanotubes with small concentration of structure defects. Moreover, sencibilization of durability properties of composites is possible only at sufficient conjugation nanotude surface with polymer molecules.

In this work were observed vibrational spectra, micro hardness, resistivity, and luminescence of poly(vinyl) chloride composites with different content of multi-walled cardon nanotubes (from 0.2 to 2.0 wt.%). The studies were performed with using Raman scattering, micro hardness, resistivity and luminescence methods. Nanotubes were obtain by chemical besieging on the dispersed catalysts. Polymer composites were produced by compressing.

It is established that durability of composites occurs only at small content of nanotubes. It proves about conjugation of nanotube surface and poly(vinyl) chloride molecules.

Modeling of electromagnetic pulse propagation through the system of carbon nanotubes

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The study has been carried out within the framework of the analysis of the dynamics of pi-electrons in a strong-coupling approximation. The dispersion law, which describes the properties of zig-zag-type nanotubes, has the form [1]:

$$E(\vec{p}) = \pm\gamma\sqrt{1+4\cos(bp_z)\cos(\pi s/m)+4\cos^2(\pi s/m)} \qquad (1)$$

For armchair-type (m, m) CNT, it has the form:

$$E(\vec{p}) = \pm\gamma\sqrt{1+4\cos(\frac{bp_z}{\sqrt{3}})\cos(\pi s/m)+4\cos^2(\frac{bp_z}{\sqrt{3}})} \qquad (2)$$

where the quasipulse $\vec{p}$ is given as (p_z, s), $s = 1,\ 2\ \ldots\ m$.

The distribution function as follows from [2] has the form:

$$f = F_0(p_z + \frac{q}{c}A_z(t))e^{-t/\tau} + \frac{1}{\tau}\int_{-\infty}^{t} e^{-(t-t')/\tau}F_0(p + \frac{q}{c}(A_z(t) - A_z(t')))dt' \qquad (3)$$

The density of $\vec{j} = (0,0,j_z)$ current is as follows: $j_z = \frac{q}{\pi\hbar S}\sum_s \int dp_z v_z f$, where $v_z = \partial E(\vec{p})/\partial p_z$ is the velocity of electrons in the conduction band.

The equation for the vector-potential in the small relaxation time approximation in SI has been obtained:

$$\frac{\partial^2 A_z}{\partial x^2} - \varepsilon_0\mu_0\frac{\partial^2 A_z}{\partial t^2} + \mu_0\frac{q}{\pi\hbar S}\sum_m c_m \sin(\frac{maq}{c}A_z(t)) = 0 \qquad (4a)$$

$$c_m = \sum_s a_{ms}b_{ms},\ b_{ms} = \int_{-q_0}^{q_0} dp_z \cos(mbp_z)F_0(\vec{p}) \qquad (4b)$$

where the integration for the zigzag-type CNT is performed with respect to the first Brillouin zone and $q_0 = \frac{2\pi\hbar}{3b}$.

We can restrict ourselves to the first three non-vanishing summands because of the depletion of c_{ms} coefficients with growing m in the sum in Eq. (4). As a result of the numerical modeling we got the tables of a_{ms} coefficients for different types of CNT.

The suggested numerical scheme allows solving the nonlinear equation (4) and forecasting the existence of nonlinear electromagnetic waves in the CNT.

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Field electron emission from ”polymer-carbon nanotubes” composites as revealed by mass spectrometry

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It seems insufficient to adequately understand molecular functioning mechanism of the carbon nanotubes, CNT, surrounded by the polymer matrix, which limits the designing of more efficient field-emission, FE, cathodes. The matrix functions are much more diverse than those supporting the CNTs in the needed position. The polymer matrix stabilizes the cathode operation protecting the tube in particular from overheating. We hope that our combined experimental instrument including TOF MS and FE-unit [1, 2] is a considerable advance in problem solving. On the example of PS(polystyrene)/MWCNT composite we show below the possibility of:

- the temperature estimation for the “emitting centre” from both the initial temperature of the PS thermal degradation and higher temperatures;
- establishing the interdependence the emission current, electric field, the actual temperature of the emitting CNT thus establishing their number;
- monitoring the emitter surface structure evolution analyzing the cathode characteristics deterioration under the electron emission;
- optimizing the pattern for new composite film with noncarbon nanofillers;
- controlling the CNT orientation immediately under emitter operation, which results in decreasing of the electric field to obtain the same emission current.

The advantage of the method is in that it allows to adequately select polymer matrix with proper thermal stability the functioning conditions and the emitter life time taken into account.

This research is supported by RFBR grant (N 09-08-01076-a) and the Physical Science Department Program of the RAS “Physics of New Materials and structures”.

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Nanosecond S-type electrical instability in carbon nanotube-polymer matrix

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Carbon nanotubes have been investigated for nanoelectronic applications. In this paper we present a preliminary study of the nanosecod voltage-current characterization on Carbon NanoTubes (CNT)-polymer matrix. For sample preparing we used the multiwall CNT in mix with TEFLON based polymer in composition 80:10 mass.%. The investigating films prepared by electrospinning-like method on Cu foel [1]. The film consist of globular structure 4-5 μm in diameter as shown in Figure 1.

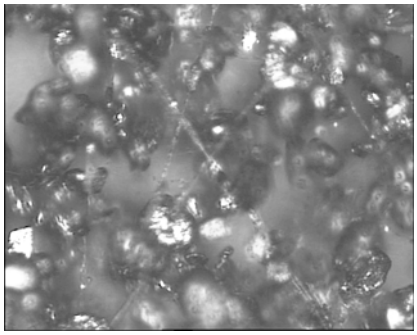

Fig.1. Microscopic view (60×70 μm) of CNT-polymer film.

We used a method for subnanosecond pulse measurements of I-V characteristics [2] with square pulses of 10 ns. Typical I-V curves with instability region (S-region) are presented in Fig. 2. The detailed shape of I-V curves near critical U_c is typical for multiwall CNTs, above U_c is ohmic, and is the result of destruction of CNT walls [3]. The statistical resistance distribution of such films was investigated.

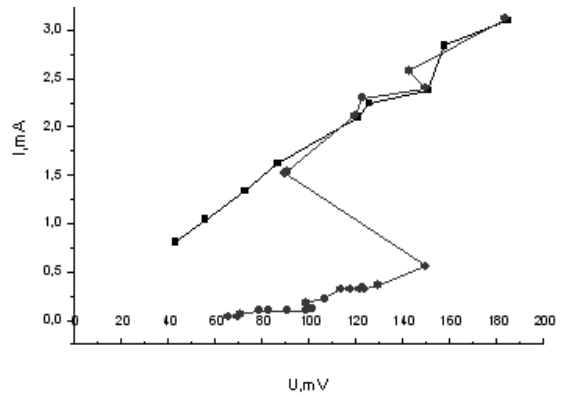

Fig. 2. Impulse I-V characteristics of CNT-polymer film.

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The semi-empirical research of chiral absorption effect of atomic and molecular particles on the carbon nanotubes surface

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Carbon nanotubes (CN) have unique mechanical, electrical and absorption properties, which are a perspective basis for creating the biochemical sensor controllers for defining the concentration of chemical and biological substances [1]. The principle of its action is based on the change of the electronic characteristics of nanotubes (the band gap, the concentration and the carrier mobility's, etc.) at the molecule sorption.

In this work the single-walled nanotubes (n, n) type (n = 3, 4, 5, 6) are considered. As the geometrical models of nanotubes the clusters (fragments) containing n six-member cycles (hexagons) on a tube perimeter and 8 - 10 elementary cells along an axis of a tube are chosen. The adsorption properties of atoms and molecules A (A = O; H_2; O_2) on carbon nanotubes are studied. The adsorption energy E_{ad}, the highest occupied (E_{HOMO}) and the lowest unoccupied (E_{LUMO}) molecular orbital energies, the band gap (E_g) and the change of the band gap caused the adsorption (ΔE_g) of the particles are calculated. The calculations of an electronic structure of the structures are carried out within the frameworks of the simple molecular cluster model [2] with the use of quantum-chemical semi-empirical schemes MNDO [2].

The analysis of the quantum-chemical calculation results has shown that the energy E_{HOMO} increases but the energy E_{LUMO} decreases with the tube diameter growth. The changes of E_{HOMO} and E_{LUMO} values indicate the changes of nanotube properties caused by the adsorption, for instance, increasing the reaction ability of the systems. The tubes with a particle adsorbed on its surface increase the CN affinity to other particles. The analysis of the band gap E_g has shown that the value of the forbidden zone decreases as a result of atoms and molecule adsorptions. It leads to the increase of CN "metallization".

The work is supported by Russian foundation of basic research (project 08-02-00663).

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Concept of single-walled carbon nanotube formation

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The investigation of carbon nanotube materials [1], which obtain by catalytic pyrolysis of ethanol, indicates about - catalyst determines structure parameters of carbon nanotube. Commonly, for carbon nanotube growing uses catalyst based-on Fe, Co, Ni [2].

To propose to obtain catalyst of carbon nanotube growing by ammonia complex of nickel precursor by sol-gel method. After formation of catalytic particles on substrate, we annealed it in vacuum. Annealing of catalyst defines the surface diffusion on substrate. So nickel particles sinters and enlarges. Therefore if we get really small particles of catalyst after annealing they will be larger. Diameter of particles defines annealing temperature and velocity of heating sample.

Particles enlarging can be suppressed by two ways. First, to dispose catalytic particles so that has a distance between any two of it more than free paths. Second, decrease just the job of surface diffusion by limited of particles motion surface.

Decreasing of precursor concentration results for increasing distance between any two of catalyst particles. In the article for example was considering standard process on the CVDomna plant [3] for precursors different concentration: $3\cdot10^{-2}$ mol/l (standard), $3\cdot10^{-3}$ mol/l, $3\cdot10^{-4}$ mol/l, $3\cdot10^{-5}$ mol/l. As result of the investigation in sample from $3\cdot10^{-5}$ mol/l was reached carbon nanotube with diameter about 2 nm by atomic-force microscopy. This dimension conforms to diameter of single-walled carbon nanotube.

Decrease of surface diffusion was reach by impregnation precursor in zeolite. The zeolite was annealed in 4 hours with 300 centigrade degrees for restoration of it by vacuum annealing. Next, zeolite was impregnated by precursor in twenty-four hours. After that was leads standard process on the CVDomna plant. As result of the investigation in zeolite sample was reached single-walled carbon nanotube by transmission electron microscopy. This dimension conforms to diameter of single-walled carbon nanotube.

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Conductivity of fullerite C_{60} and single-wall carbon nanotubes at pressures 20-50 GPa

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Conductivity of fullerite C_{60} and single-wall carbon nanotubes (SWNT) have been studied at pressures 20-50 GPa and temperatures 77-400K. The resistivity relaxation kinetics of C_{60} at changing pressure also was studied.

High pressures have been generated in the high-pressure cell with synthetic carbonado-type diamond anvils. The anvils are good conductors and can be used as electric contacts making possible to measure temperature and pressure dependences of resistance

Resistivity peculiarities were identified with the known phase transitions of fullerite. Successive phase transitions of fullerite C_{60} appeared in the course of HPHT treatment were accompanied by changes in resistance, which can be of quite different magnitude (from hundreds Ohm to hundreds MOhm) and different dependence on temperature. Critical pressures for the transitions depended on conditions and duration of preliminary HPHT treatment. This fact, as well as smeared character of the transitions are connected with long relaxation time, which was found to be of ~140 min.

Three types of SWNT samples were investigated: samples produced by the graphite thermal dispersion method (SWNT percentage is 40%), the chemical vapor deposition method (SWNT percentage is 80%) and HiPco method (SWNT percentage is 90%).

Electric properties of the samples under high pressure were dependent on SWNT percentage. The electric characteristics of SWNT samples remained of the same character with the increasing of SWNT percentage, but the additional features appeared (intermediate region on the temperature dependences of resistance; additional extremums on the baric dependences of activation energy in the pressure range of 40-45 GPa). Thus, the dependences obtained are connected with electric characteristics of SWNT, and not with the impurities contained in the sample.

The irreversible changes of the electric properties of the samples observed in the pressure range 27-45 GPa can be connected with both the structure modification and partial destruction of the sample.

This work was supported in part by the CRDF grant # Y4-P-05-16.

A prismatic modification of single-walled carbon nanotubes by fluorine and boron atoms

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At present a main electronic characteristics of carbon nanotubes are sufficiently reliable determined. However, it is important for a practice that these characteristics change in required limits. In this connection a problem of a direct modification of initial carbon nanotube structure and a prediction of their electronic properties exists.

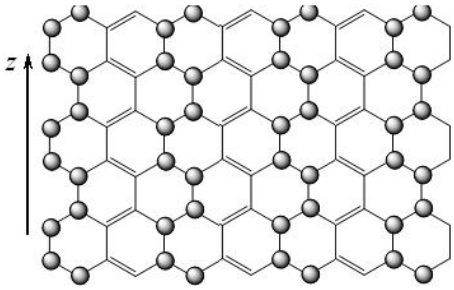

Figure 1.

In present work a modification of single-walled carbon nanotubes (SWCNT) is investigated. Two cases are considered: (a) regular adsorption of fluorine atoms along axis of nanotube; (b) regular substitution of SWCNT carbon atoms by boron atoms (b). As result of such modification a SWCNTs take a prism forms (prismatic modification). The cis-polyene chains are in the sides of these prisms obtained. A Figure 1 takes the planar presentation of prismatic modified SWCNT. An axis *z* is an axis of nanotube.

A limited length SWCNTs with hirality indexes (*n*, 0) *n*= 6, 8, 10, 12 are as an initial models used. A carbon atom number in examined models changes at 130 to 392. Calculations are performed in semiempiric AM1 scheme.

Main characteristics of energy spectra of typical SWCNT and their prismatic modifications are presented in Figure 2.

It is obtained that a SWCNT prismatic modifications as by adsorption of fluorine atoms so a substitution of carbon atoms by boron atoms lead to increase of band gap width. It is shown that an essential influence on SWCNT energy characteristics exerts a method of modification and also a planning degree of a prism sides on which a cis-polyene chains are placed.

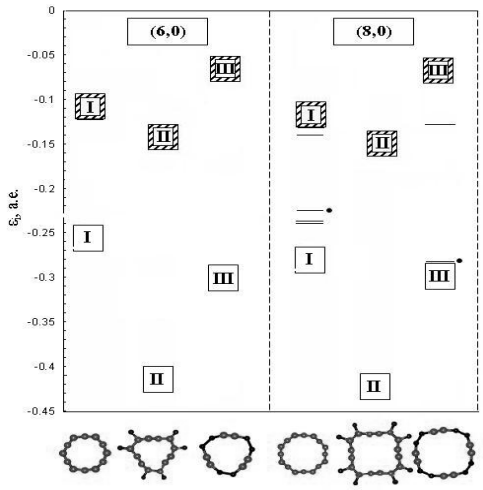

Figure 2. Energy spectra of SWCNT and their prismatic modifications. I – initial SWCNT, II – SWCNT modification (a), III – SWCNT modification (b). ▨ means lowest border of a conduction band, □ means highest border of a valence band. Isolated energy levels are touch lines presented.

A ring conjugation in a prismatic modifications of single-walled carbon nanotubes

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In present work a modification of single-walled carbon nanotubes (SWCNT) is investigated. Two cases are considered: (a) regular adsorption of fluorine atoms along axis of nanotube; (b) regular substitution of SWCNT carbon atoms by boron atoms (b). As result of such modification a SWCNT take a prism form. Isolated conjugated one-dimensional subsystems (cis-polyene chain) place in the sides of these obtained prisms. It is examined an influence of an equatorial ring conjugation connecting isolated conjugated one-dimensional subsystems on electronic properties of a modified SWCNT. A Fig. 1 takes the planar presentation of prismatic modified SWCNT with a polyacene provided an equatorial ring conjugation. An axis *z* is an axis of nanotube.

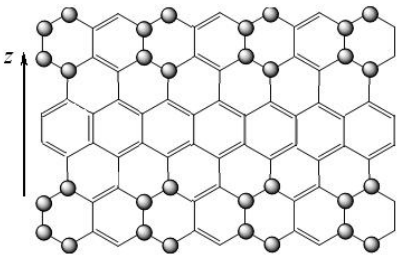

Figure 1.

A limited length SWCNTs with hirality indexes (*n*, 0) *n*= 6, 8, 10, 12 are as an initial models used. A carbon atom number in examined models changes at 130 to 392. Calculations are performed in semiempiric AM1 scheme.

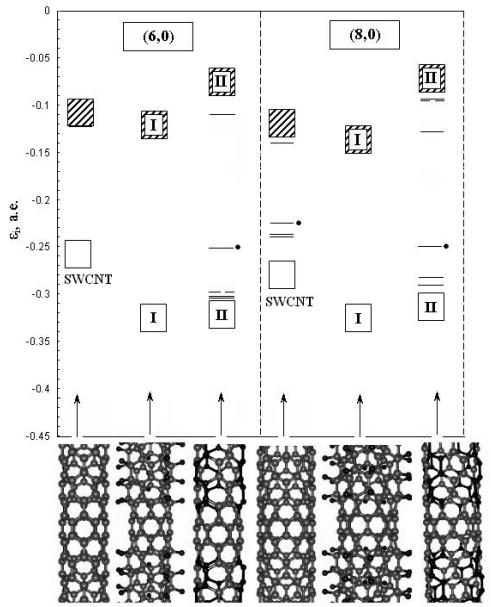

Figure 2. Energy spectra of SWCNT and their prismatic modifications. I – SWCNT modification (a), II – SWCNT modification (b). ▨ means lowest border of a conduction band, □ means highest border of a valence band. Isolated energy levels are touch lines presented.

Main characteristics of energy spectra of typical SWCNT and their prismatic modifications with an equatorial ring conjugation are on Fig.2 presented.

It is obtained that a SWCNT prismatic modifications as by adsorption of fluorine atoms so a substitution of carbon atoms by boron atoms lead to increase of band gap width. However, a band gap width in SWCNT with boron atoms is some larger a band gap width in SWCNT with fluorine atoms. It is found that isolated energy levels arise in band gap spectra of modified SWCNT. It shows that an essential influence on SWCNT energy characteristics exerts a method of modification and also a structure of equatorial ring conjugation which connects an isolated conjugated one-dimensional subsystems in a modified SWCNT.

An isolated one-dimensional conjugated subsystem in a modified single-walled carbon nanotubes

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A working of different purpose nanodevices requires an elaboration of nano-element base of which materials have necessary exploitation properties. These materials can be to obtain by direct modification of single-walled carbon nanotubes (SWCNT).

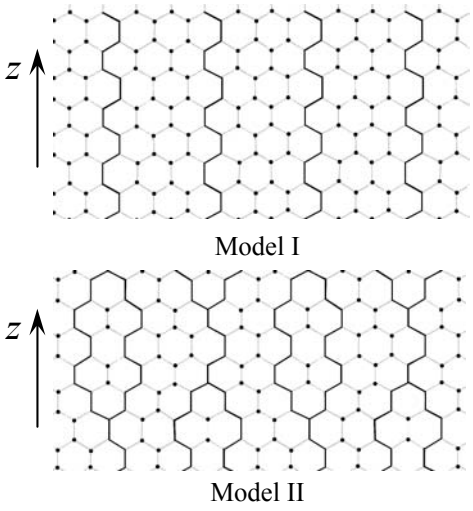

Figure 1. SWCNT carbon atoms connected with a fluorine atoms show by points.

In present work a modification of a SWCNT is carried out a regular adsorption of fluorine atoms along axis of nanonube as it shows on Fig.1. An axis *z* is an axis of nanotube. This modification leads to a formation of prisms with different structure of the sides. In the sides it can place one-dimensional isolated conjugated subsystems of cis-polyene type (Model I) and similar subsystems connected between themselves (Model II). A limited length SWCNTs with hirality indexes (*n*, 0) *n*= 6, 9, 10, 12 are as an initial models used. A carbon atom number in examined models changes at 130 to 392. Calculations are performed in semiempiric AM1 scheme.

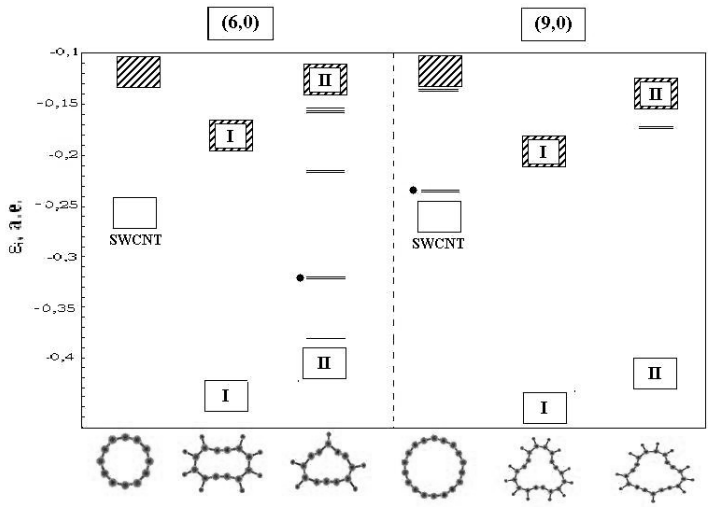

Figure 2. Energy spectra of SWCNT and their prismatic modifications. I – SWCNT modification corresponds to Model I, II – SWCNT modification corresponds to Model II. ▨ means lowest border of a conduction band, ▭ means highest border of a valence band. Isolated energy levels are touch lines presented.

Main characteristics of energy spectra of typical SWCNT and their prismatic modifications are on Fig.2 presented. It is obtained that modification of SWCNT leads to increase of a band gap width. It shows that an isolation or an unification of one-dimensional conjugated subsystems essentially influence on an electronic properties of modified SWCNTs. Like that an examined prismatic modification of a SWCNT allows to work the nanostructures with a control parameters of conducting properties.

Few cycle optical pulses in the carbon nanotubes with periodical impurities

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In this work the research of dynamics few cycle optical pulses in the carbon nanotubes are represented. Great attention is paid to a large electron`s mobility in the carbon nanotube and its unique properties which are an alternative of silicic base in the modern microelectronics [1].

The model Anderson Hamiltonian [2]:

$$H = H_h + H_{im} + H_{hyb}$$

$$H_h = -\sum_{j\Delta\sigma} t_\Delta (a^+_{j\sigma} b_{j+\Delta\sigma} + b^+_{j+\Delta\varsigma} a_{j\sigma}) + U \sum_j (a^+_{j\sigma} a_{j\sigma} a^+_{j-\sigma} a_{j-\sigma} + b^+_{j\sigma} b_{j\sigma} b^+_{j-\sigma} b_{j-\sigma})$$

$$H_{im} = \sum_j (\varepsilon d^+_{j\sigma} d_{j\sigma} + \varepsilon d^+_{j-\sigma} d_{j-\sigma} + U_1 d^+_{j\sigma} d_{j\sigma} d^+_{j-\sigma} d_{j-\sigma})$$

$$H_{hyb} = V \sum_{j\sigma} (a^+_{j\sigma} d_{j\sigma} + d^+_{j\sigma} a_{j\sigma})$$

where the $a^+_{j\sigma}, a_{j\sigma}, b^+_{j\sigma}, b_{j\sigma}$ - Fermi operators of creation and annihilation of electrons (j,σ – space and spin index), t_Δ - jumping integral (resonance integral), U – Coulomb's repulsion electrons constant, $d^+_{j\sigma}, d_{j\sigma}$ Fermi operators of creation and annihilation of impurity electrons, ε -the level of impurity energy; U_1- Coulomb's repulsion impurity electrons constant, V - overlap integral between wave functions of impurity electrons and π-electrons of carbon form zones.

In our calculations it were chosen the following parameters of Anderson Hamiltonian, appreciated by quantum-chemical method MNDO $t_\Delta \approx 2$ eV, $U \approx 12\text{eV}, U_1 \approx 12\text{eV}$, $V \approx 2\text{eV}$.

We received the dispersion law by Green functions technique. A joint dynamics of electrons and electromagnetic field has been considered in the low temperature limit and effective equation describing distribution of the few cycle optical pulses has been obtained. This equation has been solved at various parameters of our task.

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Magnetic properties of carbon nanotubes with low content of Fe

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Films of oriented carbon nanotubes (CNTs) containing different concentrations of iron (0.5%, 1%, 1.5%, 2%, 2.5% and 5%) were studied by means of SQUID and force microscory. CNTs were grown on silicon substrates in inert atmosphere at 800°C by CVD method. Magnetic measurements reveal that the easy axis of magnetization is parallel to substrate, and the difference between easy and hard magnetic directions decreases with growth of concentration of iron in the samples, while in CNTs heavily doped with iron the easy axis of magnetization is perpendicular to substrate [1]. It was suggested that magnitostatic interaction between iron grains on the tips of nanotubes with low content of iron makes them form a plate which defines magnetization pattern, and when content of iron is increased, most part of it is located inside CNTs.

We have observed the difference between Curie temperatures for H || CNT and H $\perp$CNT. Curie temperatures lie in the range 500-700K, the lower value corresponds to iron carbide, Fe_3C. The temperature gradient is higher in samples with higher concentration of iron. This result can be explained by finite size effect [2].

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