

Performance of nanocarbon field emitters in electron device relevant conditions

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Recent progress in nanotechnologies allows to expect development of competitive nanocarbon cathodes for high-voltage vacuum device applications in the nearest future. Different types of nanocarbon structures demonstrate high efficiency of field-induced electron emission: mA-scale currents are extracted from mm²-area samples in electric field of a few V/ μ m (flat gap value). Yet, the reported parameters are usually defined in conditions substantially different from the ones realized in many practical applications.

Typically, emission properties of nanocarbons are tested in narrow field gaps, with a solid anode electrode immediately opposing the emitter and receiving full electron current. In high-voltage vacuum tubes, inter-electrode gaps are usually wider (a few mm), and field configuration directs electrons outside of the field gap for utilization. The significant difference might consist in lower density and higher energy of return ion flow at the emitter in the latter case. Previously, we presumed involvement of ion bombardment in the actual mechanism of thermo-field emission activation of low-aspect-ratio multi-phase nanocarbon films [1, 2]. The present paper summarizes experimental data accumulated by our group with different forms of nanocarbon, relating to the effect of the anode and field gap configuration on emission activity establishment and maintenance. For all low-aspect-ratio materials, we observed much lower efficiency of thermal activation of emission whenever the extracted electrons were led away from the field gap.

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STM study of C₆₀ thin film growth on Bi/Si surface

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An understanding of the growth of organic thin films and nanoscale structures on Si surface is important for potential applications in micro- and optoelectronic devices exploiting the flexibility of molecular structures and properties. Among them thin films of fullerene are very promising, for example in fabrication of electro-active elements in solar cells. In addition, fullerene molecules with their closed-cage geometry and uniform size can be considered as probable candidates for use as building blocks in nanoscience applications. We present the results of our STM investigations of the earliest stages of C₆₀ film growth.

Usually, the interaction between a semiconductor surface and an adsorbed fullerene molecule is rather strong due to high concentration of dangling bonds at the surface, and may have a strong influence on the morphology of thin solid films of van der Waals-bonded C₆₀. To reduce such an interaction and allow a growth of film in a bulk-like phase we used a semimetallic Bi(001)/Si(111) template as a substrate for the RT deposition of C₆₀ [1]. The epitaxial C₆₀ film growth has been performed as substrate temperature of 150°C. Fullerene molecules deposited on well-ordered Bi films interact only weakly with the substrate through weak van der Waals forces. C₆₀ is free to diffuse on this surface and usually forms highly ordered islands even at less than one monolayer coverage but the initial nucleation of deposited molecules occurs preferentially in some regions, and these special sites can be viewed as “anchor sites”. STM observations confirmed that that most favorable sites for C₆₀ nucleation are double steps and Bi domain boundaries.

All STM images of the surface with one monolayer coverage of C₆₀ showed a characteristic modulation pattern coming from the epitaxial relation between C₆₀ and Bi (5:11) as well as the voltage dependence which is related to the charge redistribution within C₆₀ molecules. In contrary to that the STM images of thick layers of C₆₀ (4-5 monolayers) did not exhibit any manifestation of modulation while the I-V characteristics taken from these layers did not show a shift which confirms evidently the miserable charge transfer filling up the LUMO states.

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Electronic structure of fluorinated carbon nanotubes studied by X-ray absorption and photoelectron spectroscopy

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This contribution presents results of the detailed investigation of the chemical bonding and electronic structure features for the series of fluorinated multi-walled carbon nanotubes (MWNTs) with different fluorine content using X-ray absorption and photoelectron spectroscopy.

The MWNTs were obtained by arc-discharge method. They were fluorinated at a temperature of 420°C in a flow of F₂ diluted with N₂ and contained gaseous HF as catalyst. All measurements were performed with the use of synchrotron radiation at the Russian-German beamline at the BESSY II storage ring (Berlin, Germany). X-ray absorption spectra for samples of pristine MWNTs and MWNTs with different fluorine concentrations (5–55 wt.%) as well as for graphite, pentacene and C₆₀ (as test-objects) were recorded at the C 1s and F 1s absorption edges.

The C 1s and F 1s spectra show a well-defined absorption structure that is indicative of formation of chemical bonding between the fluorine and carbon atoms in MWNTs. A comparison between C 1s and F 1s spectra aligned energetically using the energy separation between F 1s and C 1s core levels shows that corresponding structures in spectra under comparison reflect electron transitions to the same unoccupied electron states which are related to chemical interaction in MWNTs. The changes in absorption structures of C K and F K spectra with fluorine concentration in MWNTs were found. The number of structures and their positions in spectra did not change with increasing of fluorine concentration in MWNTs. At the same time, the shape of C 1s spectrum modified drastically under fluorination: intensity of the peak at ~ 285 eV was reduced greatly and that of the peak at ~ 289 eV increased significantly. The C 1s absorption spectrum of MWNTs with maximum fluorine concentration was very similar to “white graphite” one.

The changes in MWNT electronic structure appeared as a result of fluorination were analyzed.

Odd electron pairing in fullerenes and carbon nanotubes

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A traditional theory of chemical bonding has taken conceptual and quantitative determination in terms of either bond indices or Wiberg indices within the framework of the single-determinant close shell restricted HF (RHF) approximation. Addressing to odd-electron systems, this corresponds to a limit case of strong coupling between the electrons. The approach generalization for systems with arbitrary coupling can be reached by taking the odd electrons spin into account. Within the single-determinant approximation, the open shell unrestricted HF (UHF) approach allows for introducing a quantitative characteristic for the odd electron interaction which is determined by the exchange integral $J = J_0 + K$ involving both Coulomb and exchange interaction. Since the Coulomb interaction dominates in the majority of cases, the integral is negative. However, when $|J|$ decreases and approaches a border value $|J_{bord}|$, both HF solutions become unstable. The UHF energy is lower than that of the RHF solution but higher than that of the pure spin (PS) solution so that the UHF state is spin-contaminated with increasing admixture of high spin states at lowering $|J|$.

Within the framework of the traditional consideration, the excess spin density of the UHF solution allows for introducing new characteristic for the system caused by *effectively unpaired electrons* (EUPEs) (K.Takatsuka, T.Fueno, K.Yamaguchi, 1978), the total number of which N_D increases when the integral $|J|$ decreases. Partitioning the N_D value over atoms forms a highly characteristic $N_{D\hat{A}}$ map, which turns out to be coincident with that one for the free valency distribution. In a certain sense, $N_{D\hat{A}}$ values highlight a hidden chemical susceptibility of the odd-electron system atoms, which later on may be disclosed in different chemical reactions. The finding gives a key to play chemistry with odd-electron systems with open eyes by performing a controllable computational synthesis of different adducts just following indication on chemical susceptibility of the system atoms presented by the corresponding $N_{D\hat{A}}$ map. The current paper presents the approach application to the chemistry of fullerenes and carbon single-wall nanotubes. For example, analyzing $N_{D\hat{A}}$ maps of different types SWNT fragments, we observed high chemical activity of bending part of nanotubes under strain treatment.

Thermal instability at the electron field emission of carbon nanotubes

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There have been established a mechanism of limitation of the emission current in carbon nanotubes (CNT) – based cathodes related to the temperature dependence of emission properties of nanotubes. This limitation has the character of a thermal instability that manifests itself in a drastically rising the emitter temperature at exceeding some magnitude of the emission current. The magnitudes of the limiting emission current vs absolute value of electrical conductivity have been determined on the basis of solution of the heat conductivity equation for an individual nanotube at various model temperature dependencies of the heat conductivity and electrical conductivity coefficients.

Dependence of conductivity of double wall carbon nanotubes on inter-layer location and its longitude

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Carbon nanotubes (CNT) with their unique electronic and mechanical characteristics begin to play a large role as construction blocks of electronics in XXI century [1].

The theoretical calculations of the conductivity of double wall carbon nanotubes (DWNT) have been carried out within the framework of Hubbard's model which include among the sum of the separate subsystem energy operators. The model Hamiltonian includes the energies of electron jumping between the next carbon atoms and between layers of DWNT and the energy of Coulomb interaction of electrons locating on the same crystal unit [2]. Further the Heisenberg's equations of the operator movement have been solved within the framework the method of the Green's functions. The conductivity tensor has been calculated by Green's functions of the current density according Kubo's formula [3].

The four various configurations of mutual locations of layers meeting the requirements of high symmetry of DWNT with commensurable non-chiral walls were taken up. Also the external layer long has modified from 50 nm to 5000 nm and their diameter has modified from 1.1 nm to 1.5 nm.

Besides the effect of the change of conductivity character of DWNTs has been found. Thus the plateau has been observed on the conductivity curve in an interval of temperatures 60-120 K. Also it has been obtained that the plateau value decreases with the tube diameter increase.

The change of mutual locations of DWNT layers doesn't influence on the character of dependence of conductivity. However the configuration which doesn't have diagonal crossings between DWNT layers gives a drastic decrease of conductivity. This is bound up with location of layers which isn't advantageous energy. It conforms to the maximum potential surface of the interaction layers energy. The amplitude of conductivity change in case other mutual locations has volume approximately 20% from middle mutual locations.

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The temperature dependence of the tensor of proton conductivity of single-wall nanotubes

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The main idea of this work is calculations of the tensor of proton conductivity of the single-wall carbon nanotubes (SWNT) [1]. In this work has researched opportunity for using the “arm-chair” and “zig-zag” SWNTs as materials with the proton conductivity. An semi-empirical quantum chemical calculation of the process of transportation of the proton on surface of the SWNTs has made [2]. The jumping mechanism of transportation of ion H^+ from one atom of carbon to another along C-C connection for the “arm-chair” and “zig-zag” SWNTs has taken up.

It has received the temperature dependence of the lengthwise isotropic conductivity $\sigma(T)$ the SWNTs. The theoretical calculations have been carried out within the framework of Hubbard’s model and method of the Green’s functions [3]. The model Hamiltonian:

$$H = - \sum_{j\Delta s} t_{\Delta} \left(a_{js}^+ a_{j+\Delta s} + a_{j+\Delta s}^+ a_{js} \right)$$

where t_{Δ} - jumping integral (resonance integral), the $a_{js}^+(t)$ and $a_{js}(t)$ - Fermi operators of creation and annihilation of a proton on j point with spin s , Δ - inter-atomic distance. The meanings of resonance integral were received by Simpson’s method with basis of wave function of harmonic oscillator.

The results of the research are dependences of the proton conductivity from the temperature:

$$\sigma = \frac{e^2}{2pKTV} \sum_q \int_{-p/a}^{p/a} \left[\mp \frac{1}{\hbar} \sqrt{3} g_0 a_0 \frac{dE(k)}{dk} \right]^2 \cdot \left(\exp \left[\frac{E(k)}{kT} \right] + 1 \right)^{-1} dk,$$

where $a_0 = 1.44 \text{ \AA}$, $N_y \sqrt{3} a_0 k = 2q\mathbf{p}$, $q = 1, \dots, N_y$, $-\frac{\mathbf{p}}{\sqrt{3}} < ka_0 < \frac{\mathbf{p}}{\sqrt{3}}$.

The dependences $\sigma(T)$ have the typical behavior for the semiconductors. In other words their conductivity increases with the increase of the temperature. The dependences of the “arm-chair” SWNTs and “zig-zag” SWNTs are different from each other. It is possible to justify on the basis of the differ size of the potential barrier. The potential barrier of the “arm-chair” SWNTs is twice much as the potential barrier of the “zig-zag” SWNTs. This result was expected as the concentration of the protons is low level.

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Influence of inter-layer rotation on phonon spectrum of double wall carbon nanotubes

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This work is devoted to theoretical research of inter-layer rotation influence on the phonon spectrum of double wall carbon nanotubes (DWNTs). The “arm-chair” and “zig-zag” DWNTs simulated by idealized ABAB interlayer structure have been studied earlier [1]. The stable interlayer distance and carbon-carbon bond length have been defined to be equal to 3.4 Å and 1.44 Å (obtained in semi-empirical calculations previously) accordingly. For study of specialties of phonon spectrum caused by relative rotation of carbon walls we simulated four high symmetry geometry configurations of DWNTs.

Hamiltonians of DWNT in each high symmetry configurations have been considered in harmonious approximation and the Heisenberg’s equations of movement have been solved by the use of plane waves. The algebraic dispersion equations of the fourth order on frequency square have been obtained and solved.

The circumstantial analysis of the analytically results received has shown that the phonon spectrum of DWNTs also consists of acoustical and optical branches as it was waited for. It has been found that the spectrum doesn’t contain the gap between acoustical and optical branches. Besides that the density of phonon states was changed a little, frequency pick was shifted in optical band direction.

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High current density field electron emission from carbon nanotube emitters accompanied by stable radiation of light from nanotubes

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Carbon nanotube field electron emitters are very promising for usage in various electron devices such as microwave amplifiers, flat panel displays, X-ray tubes and some others. Such emitters to be used in microwave amplifiers should be characterized by high current density, at least about several hundreds of mA/cm². We have developed high current density field electron emitters based on carbon nanotubes and have found that the high density emission current is accompanied by stable radiation of light from carbon nanotubes. This radiation is connected with thermal heating of nanotubes by the emission current up to temperatures higher than 1000°C [1]. We suppose that the high temperature keeps the surface of nanotube tips in a clean state that results in the high stability of the field emission that we observed at high current densities.

Carbon nanotube field emitters were grown by the CVD method on Si substrates with Ni as a catalyst. The emitter is a circle 0.3 mm in diameter. Its area $\approx 7 \cdot 10^{-4}$ cm². Investigations of the field electron emission were fulfilled in an ultra high vacuum chamber ($p \sim 10^{-9}$ Torr) using spherical or hemispherical stainless steel anodes 2 mm in diameter. The stable emission current $I \approx 700$ μ A (current density $j \approx 1$ A/cm²) was observed at the average electric field $E_{av} = 8$ V/ μ m. The relative current fluctuations were about 0.1%.

The orange light radiation from nanotubes was clearly seen by the naked eye and was photographed with the help of a digital reflex camera equipped with macrolens. The light spot appeared at current densities $j \approx 150$ – 200 mA/cm² and became brighter as the current was increased. The analysis of the image has shown that the size of the region that radiates light is less than the size of the carbon nanotube layer measured with the help of a scanning electron microscope, i.e. really the density of emission current is higher than calculated out of the area of this layer. So, the light radiation at high current densities visualizes the region of carbon nanotube layer that emits current.

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