Using electrostatic energy analyzer of a plane of symmetry for recording field emission spectra from carbon nanotube array

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Abstract. In this paper, the possibility is discussed of using electron emission spectroscopy to study low voltage field emission phenomenon. While using an electrostatic electron energy analyzer with the plane of symmetry, electron energy spectra were recorded with the energy resolution of $\Delta E \approx 10^{-30}$ meV. The energy analysis has been done of the electrons emitted from the array of nanotubes produced by CVD method. The conclusion is that the low-voltage emission is local and that it is caused by very strong and inhomogeneous electron field produced by surface charged defects.

1. Introduction
One of the unique features of nanostructures, including carbon nanotubes (CNTs), is the ability to emit electrons at room temperature in electrostatic fields thousands of times weaker than the values typical of field emission from a flat metal surface. To explain this phenomenon, different models have been developed, based on several fundamental principles.

In [1], the two-stage transition of electrons from CNT to vacuum is considered. The intermediate stage is some surface energy levels that are above the Fermi level of the nanostructure itself. The two stages lead to the fact that on the way to the vacuum the electron does not tunnel through one, relatively wide, potential barrier, but successively through two thinner and more transparent barriers. As a result, the probability of tunneling increases, and the threshold field strength decreases. Additional surface levels can arise both from breaking bonds of atoms on the surface or at the end of the CNT, and also out of the presence of foreign atoms adsorbed on the surface.

Another mechanism is based on the fact that due to the large aspect ratio (the ratio of the length of a nanotube to its diameter), the effect of field enhancement near the end of the CNT [2, 3] appears. However, this field amplification may be insignificant in an array of nanotubes due to their mutual shielding.

In a number of papers, it is assumed that the nanostructures can initially have a very small work function, measured in tenths of an electron volt, or even negative electron affinity [4, 5]. In particular, for linear-chain carbon fibers, the work function values of the order of 0.4 eV [6] are given.

In case of thin emitting island films, the idea is proposed of lateral acceleration of electrons skipping from island to island [7, 8]. During this movement, the electron gains energy. Then, it achieves the "emissive island" whose energy structure makes the particle change its moment direction and emit.

Since the type and features of energy spectrum of the emitted electrons are directly related to the physical nature of the emission, recording and studying emission energy spectra can make it clearer...
what processes lead to the surprising phenomenon of low-voltage field emission. To get this knowledge, the appropriate resolution of the analyzing instrument is obviously necessary. The purpose of this work is to demonstrate the possibility of studying the phenomenon of low-field emission using the spectra of emitted electrons recorded by means of a precision energy analyzer (spectrometer).

In [9], a new electron spectrometer, designed specifically to record the energy spectra and study the nature of low-field emission, is described. The main element of it is the original electrostatic energy analyzer with a plane of symmetry [10]. Due to its high energy dispersion, approximately an order of magnitude greater than the dispersion of traditional (spherical or cylindrical) electrostatic systems, the spectrometer generally achieves resolution of about $10^5$, and the corresponding absolute energy resolution of about 10-30 meV. Since the field-emission current is very unstable in time, initially the spectrometer was tuned using a thermal emitter [9]. In this paper, we present the results of the first experiments on recording the emission spectra from a CNT array.

2. Brief description of the experimental procedure
The spectrometer, a detailed description of which can be found in [9], consists of the analyzer itself, the input retarding lens at the input of the analyzer and the secondary electron multiplier at the exit of the analyzer. The field strength because of which electrons are extracted from the sample, $F=U/h$ where $U$ is the potential between the sample and the lens flat butt, and $h$ is the distance between them. Typically, $0.5 \text{ mm} < h < 2 \text{ mm}$.

Varying the potentials of the lens electrodes and the sample, it was possible to change $F$, lens focusing properties and the analyzer pass energy $E_p$, together with the corresponding energy resolution $\Delta E$. The registration of the spectra was performed in the single electron counting mode. The intensity of the recorded flux could be varied in the range $10 < I < 10^5 \text{ el./sec}$. While recording the current-voltage characteristics of the emitter, the electron flux was measured which came to the round flat butt of the lens with the diameter of 3 mm.

The samples under investigation were vertical arrays of nanotubes made using CVD procedure on the equipment of the Firstnano Easytube 2000 company and kindly provided by the state-owned company Cryosystems.

3. Experimental results
Figure 1 shows two current-voltage dependencies of the sample obtained at temperatures $T = 20 \ ^\circ\text{C}$ and $300 \ ^\circ\text{C}$. Since the emission current varied greatly over the time of measuring, each IVC is represented by two curves corresponding to the maximum and minimum currents for each fixed value of the field strength $F$. The following features of the IVCs are characteristic.

![Figure 1. Current-voltage characteristics of the sample, taken at different temperatures $T$:
The two lower curves with round nodes - $T = 20 \ ^\circ\text{C};$
The two upper curves with nodes in the form of triangles - $T = 300 \ ^\circ\text{C};$
For each temperature, the upper curve corresponds to the maximum, and the lower curve corresponds to the minimum of the detected current.](image-url)
The typical range of current oscillations during the entire time of registration was ±15–20% of the mean value. There were fast changes observed, with a rise or fall characteristic time of the order of a few seconds, and slow changes occurring in tens of seconds and even in minutes. At the same time, the current grows irregularly with increasing $F$; on the curves, there are areas of slower growth and even fall of the current.

When the temperature was risen by 280 °C, the emission threshold (field strength at which the current was equal to 0.5 nA) shifted slightly, from about 160 to approximately 140 V/mm (this is not seen in the plots). The magnitudes of the currents at high field strengths ($F > 300$ V/mm) also differ slightly for different temperatures. Only the middle part of the IVC strongly bent upwards with rising temperature. For example, at $F = 275$ V/mm, the emission current registered at room temperature varied in the region $I = 650-1100$ nA, while at $T = 300$ °C $I = 7.3-9.5$ mA.

**Figure 2.** Field emission spectra registered one after another under the following conditions: the pulling field strength $F = 175$ V/mm; emission current $5 < I < 10$ nA; sample temperature $T = 20$ °C; recording time of each spectrum $t = 50$ sec.

Figure 2 demonstrates a typical spectrum obtained at the intensity of pulling field $F = 175$ V/mm and the analyzer pass energy $E_p = 20$ eV. The spectrum was recorded twice to reduce the possible influence on its form from random chaotic variations of the emission current. The recording time of each curve was 50 sec, the emission current $I$ ranged from 5 to 10 nA.

**Figure 3.** A field emission spectrum recorded under the following conditions: field strength $F = 156$ V/mm; emission current $I < 1$ nA; sample temperature $T = 20$ °C; the spectrum recording time $t = 200$ sec.

The total width of the spectrum is approximately 0.5 eV. Characteristic are two circumstances. First, the shape of the spectrum is clearly asymmetric, with a relatively "steep" low-voltage and "flat"
high-voltage boundary. Secondly, quite regularly located peaks with an average distance between adjacent peaks of about 80–120 meV are observed on the "flat" area.

The spectrum in figure 2 can be called "integral": the relatively high emission current and energy width of the spectrum suggest that many nanotubes were emitting simultaneously. Lowering the emission current by lowering \( U \), made it possible to record the "local" emission spectrum of one or several tubes. Figure 3 shows the bifurcated emission peak with FWHM \( \Delta U_{1/2} = 18 \) meV.

Figure 4. Field emission spectra registered under the following conditions: (a) \( F = 198 \) V/mm; \( 9 < I < 13 \) nA; \( T = 20 \) °C; \( t = 120 \) sec for each spectrum; (b) \( F = 168 \) V/mm; \( 10 < I < 110 \) nA; \( T = 300 \) °C; \( t = 60 \) sec for each spectrum.

Spectra could change with the lapse of time. Figure 4 presents two ways of how the appearance of the emission spectrum changed in time. If initially (the lower curves in both graphs) either the energy structure was not completely visible (figure 4(b)) or it was only weakly marked (figure 4(a)), then, in 1-2 minutes, the emission peaks were clearly indicated. Another variant of changing the type of spectrum is shown in figure 5, where it can be seen that during the time, measured in tens of seconds, some parts of the spectrum disappeared (for example, a section around 25.15 eV or 25.33 eV) and at the same time electron currents with other energies appeared (for example in the area from 25.19 to 25.29 eV).

Figure 5. Field emission spectra registered one after another under the following conditions: \( F = 161 \) V/mm; \( 20 < I < 90 \) nA; \( T = 300 \) °C; \( t = 80 \) sec.
4. Discussion
First of all, we note that the samples under study consisted of practically homogeneous arrays of oriented and closely adjacent to each other nanotubes without any significant difference in their longitudinal sizes. In other words, with the exception of statistically determined projections, the specified CNT ensemble was located within the common border of the sample, without any noticeable protrusions. Consequently, it is not necessary to expect that the origin of field emission at a very low field strength \( F = 150–300 \) V/mm can be associated with a large aspect ratio of the emitter. The assumption of local heating of the ends of nanotubes \([11, 12]\), which leads to thermal emission, would also be unfounded, since all the spectra were recorded at emission currents not exceeding 100 nA. Further, the spectra were located in the energy region shifted relative to the energy analyzer tuning region by 2–3 eV, from which it follows that 2-3 volts of the applied voltage fell along the length of the nanotubes. Due to this circumstance, it was practically impossible to determine the position of the emitter Fermi level. Since the magnitude of the shift did not depend on the absolute value of the emission current, it should be assumed that such a spectrum shift was not ohmic. When the temperature varied within 20–300 °C, the spectrum did not change in principle; the width of the features of its fine structure at any temperature was 15–25 meV. From this we can conclude that the emission did not come from energy zones, but from narrow levels, the width of which is determined not by temperature, but by the band structure of a micro-object (a specific nanotube). The true width of any particular emission level, apparently, cannot be determined at the current level of experimental technology, because, according to calculations, the achievable spectrometer resolution is not better than 12 meV. The spectrum shown in figure 3, resembles a "stepped" spectrum \([13]\) in shape, with the only difference that the neighboring peaks are offset from each other not by 35–55 meV, but approximately by 80 meV. The envelope of figure 3 "integral" spectrum reminds the spectra received in \([11]\) but again with the only difference. In \([11]\), "flat" spectrum part is low-voltage with the "steep" high-voltage area, while in figure 3 the envelope shape is converted: "steep" slope is the low-voltage one. Probably, such a modification of the spectrum shape is related to the difference in the conditions in which the emission centers are located. In case of an individual nanotube \([11]\), there exists significant geometrical field amplification which stimulates efficient tunneling of low-energy electrons into vacuum, while in case of a nanotube array, emission can take place due to the initially lowered work function of the sample. The low-field emission efficiency of the samples under study can be explained by the presence of a concentrated positive charge on the initially defective surface of the grown structure. The principal possibility of such a charge density distribution was first indicated in \([14]\), where the anisotropy of the work function of solids was discussed. The reason for the change in the surface potential is as follows: to minimize the potential energy, the electron density tends to follow a smooth interface. Of course, this circumstance leads primarily to the appearance of a double electric layer, in which the potential drop decreases the work function. The corresponding average change in the electron potential energy at the surface \( \Delta U_s \) depends on the concentration of charged defects \( N_s \) and on the magnitude of the moment of induced dipoles \( p \):

\[
\Delta U_s = -4\pi eN_sp.
\]

For singly charged surface defects (for instance, statistically randomly distributed protrusions) with a size of the order of the diameter of the nanotubes (i.e., about 1 nm) and close to the maximum values \( 10^{12} \) cm\(^{-2}\) of their concentration, the rough estimate by formula (1) gives an average potential energy decrease of about 0.1 eV, which, however, is many times smaller than the work function of graphite-like structures. But local changes in potential with the same parameters of the system turn out to be more serious, since near such charged surface defects the electric field strength \( F_{fe} \) reaches a value of \( 10^7 \) V/cm. At such fields, the Schottky reduction of the surface barrier \( \sqrt{e^3F_{fe}} \) is of the order of
electron-volt. Thus, under these conditions, it is quite possible that an effective above-barrier emission of electrons in relatively small external fields is possible from a fraction of the surface immediately adjacent to charged defects. The observed significant (about 20%) instability of the emission current in time is probably related to the processes of recharging surface defects and to the change in their screening conditions when the surface electronic states are filled. The latter feature is explained by the difference in the parameters of the surface chaotic potential for different degrees of localization of a two-dimensional electron gas \[15, 16\]. In the limiting case of a nonconducting surface, the amplitude of the chaotic potential practically depends only on the concentration of charged defects:

$$\delta U_s \approx e^2 \sqrt{N_s}.$$  

Calculation by the formula (2) for the previously specified values \(N_s\) leads to values that are in the order-of-magnitude agreement comparable to the value of the average change in the potential energy of electrons at the surface. In the case of a high density delocalized surface electron gas (the case of a conducting surface), the amplitude of the chaotic potential is inversely proportional to the density of surface states and turns out to be several orders of magnitude smaller. Thus, as the surface states are filled (or emptied) while electric current flows, characteristic fluctuations of the height of the surface barrier may coincide with the values calculated by formula (2). Obviously, with such potential fluctuations, the corresponding instability of the emission current will be observed.

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**References**

[1] Arkhipov A V, Gabdullin P G, Gnuchev N M, Davydov S N and Krel S I 2014 Field-Induced Electron Emission from Nanoporous Carbon *Journal of Nanomaterials* 190232

[2] De Heer W A, Chatelain A and Ugarte D 1995 *Science* **270** 1179

[3] Eletskii A V 2010 *UFN* **180**(9) 897

[4] Himpsel F J, Knapp J A, VanVechen J A and 5vc Eastman D E 1979 *Phys. Rev.* **20** 624

[5] Pate B B 1986 *Surface Science* **165** 83

[6] Korobova Yu G, Babaev V G, Khvostov V V and Guseva M V 2008 *Moscow University Physics Bulletin* **1** 33-38

[7] Arkhipov A V, Zhurkin A M, Kvashenkina O E, Osipov V S and Gabdullin P G 2018 *Nanosystems: physics, chemistry, mathematics* **9**(1) 110-113

[8] Andronov A, Budyлина E, Shkitun P, Gabdullin P, Gnuchev N, Kvashenkina O and Arkhipov A 2018 *J. Vac. Sci. Technol. B* **36**(2)

[9] Bondarenko V B, Davydov S N, Gabdullin P G, Gnuchev N M, Maslevtsov A V and Arkhipov A A 2016 *St.Petersburg State Polytechnical University Journal: Physics and Mathematics* **4**(253) 94-106

[10] Davydov S N, Kudinov Yu A, Golikov Yu K and Korablyev V V 1995 *J. Electron Spectrosc. Relat. Phenom.* **72** 317-321

[11] Purcell S T, Vincent P, Journet C and Vu Thien Binh 2002 *Phys. Rev. Lett.* **88** 105502

[12] Bocharov G S and Eletskii A V 2007 *Technical Physics* **52**(4) 498-503

[13] Lobanov V M and Sheshin E P 2006 *Technical Physics Letters* **32**(12) 1074-1081

[14] Smoluchowski R 1941 *Phys. Rev.* **60** 661

[15] Bondarenko V B, Kuz’min M V and Korablyev V V 2001 *Semiconductors* **35**(8) 927

[16] Bondarenko V B, Davydov S N and Filimonov A V 2010 *Semiconductors* **44**(1) 41-44