Emission properties of carbon nanotubes and cathodes on their basis

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Introduction. Carbon nanotubes (CNT) are elongated cylindrical structures ranging from one to several tens of nanometers in diameter and up to several micrometers in length, consisting of one or several hexagonal graphitic layers rolled into a tube. A nanotube is ended usually with a hemispherical cap which can be considered as half of a fullerene molecule. However, as distinct from fullerenes which are a molecular modification of carbon, CNTs combine the properties of both molecules and the solid state and can be considered as an intermediate state of the substance (between molecular and condensed ones). This peculiarity attracts the continuously rising interest of researchers addressed to the exploration of fundamental peculiarities in the behavior of such an exotic object in various conditions. In the last few years one could observe a real boom of investigations directed to production, establishing physical and chemical properties and determining ways for the most effective practical application of CNTs. Thousands of papers are published on this subject every year. These investigations have resulted in a quick change in our notion about the mechanisms of synthesis of CNTs in various experimental conditions, about their structural features and physical and chemical behavior, and also about possible applications. For this reason the author's review article devoted to the emission properties of carbon nanotubes [1], published in Physics-Uspekhi about 6 years ago, has become rather antiquated and now is of only historical interest.

Carbon nanotubes are believed to be discovered by Iijima [2] (1991) while elongated carbon structures of nanometer diameter were observed and reported well before [3 – 5]. CNT’s combine happily miniature size, good electrical conductivity, extraordinary strength, high mechanical, chemical and thermal stability which make them an attractive object of nanoindustry.

An important basic property of CNTs relates to their high aspect ratio, due to which the electric field strength in the vicinity of the nanotube's cap is hundreds times higher than the relevant volumetrically averaged magnitude of that generated by an external source. This in its turn results in an extraordinarily high value of the electron emission current at a relatively low applied voltage [6 - 8]. Therefore, the electron field emitters with CNT-containing cathodes are beyond comparison with other field emission devices. Flat panel displays [9 - 11], cathode ray lighting tubes [12], x-ray sources [13-15] and microwave amplifiers [16, 17] fall in this category. By this means the development of CNT-based emitters results in the creation of a new class of electronic devices distinguished by their extraordinary small lateral sizes and comparatively low magnitude of power voltage. This report describes the physical principles forming the basis of CNT-based field emission cathodes, the natural limitations of their operation characteristics related to the electrical field screening effects, thermal effects and statistical spread in emission properties of individual CNT’s. Recent advances in development and design of specific devices utilizing CNT-based cathodes are described.

Fowler-Nordheim equation. The phenomenon of the electron field emission is based on the quantum tunneling of an electron found in a conductor under the action of an external electrical field [18]. A simple quantum mechanical approach results in the electrical field dependence of the electron emission current density $J$ that is called as the Fowler-Nordheim (FN) equation [18]:

$$J = C_1 E^2 \exp \left( -\frac{C_2^2}{E} \right) = 1.6 \times 10^8 \left( \frac{E^2}{\phi} \right) \exp \left[ -\frac{6.8\phi^{3/2}}{E} \right] \text{A/cm}^2,$$

where $C_1$ and $C_2$ are dimensional coefficients, $E$ (V/nm) is the electrical field strength on the emitting surface and $\phi$(eV) is the work function of the emitter material. The total emission current is expressed by integrating the current density (1) over the emitting area: $i = \int J \text{d}S$. 
Due to approximate character of the FN equation that does not take into account the specific band origin of the conductor under investigation and some details of its crystal structure, the convenient way for treatment of experimental data by usage of this equation consists in the logarithm representation of a current-voltage emission characteristic. In doing so, there is a linear proportionality between $\ln(J/E^2)$ and the inversed magnitude of the electrical field strength $1/E$. The linear character of this dependence implies the electron field origin of the emission observed, the slope of it contains indications to the magnitude of the electrical field on the conductor surface and the absolute value of the emission current permits one to evaluate the area of the emitting surface. Such a representation is of a special importance in the case of CNT-based emitters, because the magnitude of the electrical field strength on the nanotube’s tip can exceed considerably the average magnitude determined as the applied voltage divided by the inter-electrode gap. The reason of this difference is the electrical field enhancement phenomenon considered in detail below. The electrical field enhancement factor $\beta$ determined as the ratio of the real field magnitude $E$ to the average one $E_o$ ($\beta = E/E_o$) can reach very large values for CNT’s (see below). Therefore one should use the amplified magnitude of the electrical field strength $E$ utilizing Eq. (1) while processing experimental data. Numerous measurements performed have shown that the emission properties of both individual CNT’s and well aligned massif of those obey to the FN equation in a wide range of the electric currents. This is illustrated by the current-voltage characteristic of NTs measured inside the FE-SEM in Ref. [19] (fig. 1).

**Electrical field amplification.** The most important feature of CNT’s in terms of their emission properties is their high aspect ratio (the ratio of the length $l$ to diameter $d$). Due to this peculiarity the magnitude of the electrical field on the surface of the tip of a vertically aligned individual nanotube exceeds approximately $l/d$ times the average magnitude determined as the ratio of the voltage applied $V$ to the distance between the nanotube’s tip and the anode. Since the aspect ratio for CNT’s can reach $10^3$ and more, the electron field emission of CNT occurs at much lower magnitudes of applied voltage comparing to conventional electron field emitters. This offers a possibility for development of a new generation of vacuum electron devices distinguishing in a reduced level of applied voltage and power supply. The dependence of the electrical field amplification factor on the geometry of a CNT can be evaluated on the basis of electrostatic calculations.

The most accepted way to determination of the electrical field amplification factor for CNT’s consists in the numerical solution of the Laplace equation in the vicinity of a grounded CNT experienced by the action of the external electrical field. The spacial distribution of the electrical potential determined on the basis of this solution permits one to evaluate the electrical field strength in all the region of the inter-electrode gap and therefore to find the electrical field amplification factor that is defined as the ratio $\beta = E_s/E_{av}$ ($E_s$ is the electrical field at the apex of the nanotube and $E_{av}$ is the average electrical field determined as $E_{av} = U/L$; $L$ is the inter-electrode distance). An example of such a calculation is illustrated on fig. 2 where the dependence of the $\beta$ factor on the aspect ratio of a CNT modeled by a cylinder with a flat cap [20] is compared with that obtained by modeling a nanotube through stacked identical conducting spheres [21]. At high aspect ratios, the curves are seen to diverge, which can be explained by different approaches to modeling the nanotube structure.
Screening effects. The character of the electrical field enhancement depends crucially on the density of CNT's in a massif. Indeed in the case of a homogeneous dense massif of closely spaced vertically aligned CNT's the electric potential produced by an external electrode is screened by the neighboring nanotubes so that the electrical field amplification is negligible and $\beta \approx 1$. As the density of CNTs is lowered the amplification factor rises reaching its maximum value when the inter-tube distance exceeds considerably the height of a nanotube. The emission current density is proportional to the density of nanotubes and rises sharply with $\beta$. Therefore the emission current density is a non-monotone function of the inter-tube spacing $S$ reaching its maximum magnitude at about $S \approx h$. This dependence has been evaluated numerically by the authors [20, 22] within the frame of a simple model statement on the basis of solution of 3D Poisson equation for a massif of varied density. The calculation results [20] are shown on fig.3 presenting the dependencies of the amplification factor and the emission current density on the inter-tube spacing. In distinction to Ref. [22], where the optimum inter-tube spacing is close to $2h$, the calculations [22] resulted in $S_{\text{opt}} \approx 0.5h$.

Statistical spread in CNT parameters. High sensitivity of emission properties of CNTs to their parameters such as height, diameter, work function etc. causes a notable deviation of the I-V characteristics of a CNT massif from the FN dependence (1) inherent to an individual CNT. A simple approach illustrating the influence of a statistical spread on the I-V characteristics of a CNT-based cathode have been developed in Ref. [23, 24] where the electrical field amplification factor $\beta$ of individual nanotubes involved into a massif
was assumed to be spread in a statistical manner obeying the normal distribution. Averaging the FN equation with this normal distribution has resulted in a generalization of the FN dependence in the following form:

$$\ln \frac{J}{E_o^2} = \ln (C_0 \beta_o^2) - \frac{C_2}{\beta_o E_o} + \frac{C_1^2 (\Delta \beta)^2}{4 \beta_o^2 E_o^2}. \tag{2}$$

The dependence (2) is compared on Fig. 4 with the experimental I-V dependence drawn in FN coordinates [24]. As is seen a good agreement is reached setting the relative spread $\Delta \gamma / \gamma_0 = 0.304$.

Fig. 4. I-V characteristics of a CNT-based cathode measured by the authors of Ref. [24] (points) and calculated on the basis of approximate relation (2) [23] (solid line). The broken line corresponds to the FN equation.

References