Modeling of stochastic processes in the emission characteristics of multitips electron sources

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Abstract. In this work, the modeling of the fluctuations in the current-voltage characteristics of the multi-tip field emitter was produced using adsorption/desorption theory principles. The model is based on two-component emitter with emission sites, which have two different work functions: with adsorbed particles and without ones. As a result, the cloud type fluctuations in the SK-diagram were generated and the histogram of the effective field enhancement factor was plotted. Obtained dependences was similar to the experimental ones.

1. Introduction

In the last two decades scientists have shown an increased interest in the possibility of creating a new class of instruments based on a multi-tip field emitters with elongated nanostructures at the surface. One of the promising areas of corresponding development are emitters based on conducting carbon nanotubes (CNTs) fixed in a layer of dielectric polymer [1]. The study of their properties and optimization of the field emitter technology are associated with a number of difficulties: irregularity of the emission sites location, stochastic spread of their effective heights, interaction between neighboring sites, and adsorption-desorption processes occurring under technical vacuum conditions (~10\(^{-7}\) Torr) [2, 3]. In this regard, the study of the relationship between the emitter morphology, its electrophysical properties and vacuum conditions is an actual problem. One approach to this task is the computer simulation of the multi-tip field emitter characteristics, which makes it possible to reveal the main regularities of stochastic processes on the emitter surface [4]. This can be the key to understanding and subsequent controlling of the electrical vacuum devices based on carbon nanotubes.

In our previous work we have shown the principal possibility of obtaining by computer simulation methods a complex forms of current-voltage characteristic (IVC) which are close to IVCs observed in the real experiments [5]. Here we describe the simulation of the experimental IVC fluctuations for the multi-tip field cathode. The model is based on adsorption-desorption processes. As a platform for modeling the LabVIEW software was used.

2. Model

It is known that at the high vacuum the main role of adsorbents is played by the particles H, H\(_2\), O, O\(_2\), N, N\(_2\), CO, CO\(_2\) and H\(_2\)O. Theoretical calculations in conjunction with experimental data show that H, H\(_2\) and H\(_2\)O improve the emission, whereas O, O\(_2\), CO and CO\(_2\) deteriorate it by increasing the work function of nanotubes [6-8]. Moreover, hydrogen leaves CNTs surface quite easily when the cathode is heated and the particles O and CO are fixed more firmly on the CNT surface [9]. Nitrogen (N and N\(_2\))...
reduces the work function very weakly so its influence can be neglected on the background of other volatile products. Under the technical vacuum and under the conditions of electron-stimulated desorption of particles from the anode, the effect of particles containing oxygen (O, O₂, CO, and CO₂) is enhanced [10]. On the other hand, sufficient Joule heating of the emission surface can lead to the removal of the adsorbed particles from the emission surface and to increase in the stability of the entire emission pattern of the cathode as a whole [11].

The developed model is based on the probabilistic laws of adsorption and desorption of particles from the cathode surface, as well as on electron-stimulated desorption of particles from the anode and change in particle concentration in the interelectrode gap due to the operation of vacuum pumps.

According to the classical concepts about desorption, the rate of change in the degree of coating of the surfaces with adsorbates (in our case of the cathode) is expressed with the difference of the adsorption rate \( v_a \) and the desorption rate \( v_d \) [12]:

\[
\frac{d\theta}{dt} = v_a - v_d, \tag{1}
\]

\[
v_a = (1 - \theta)k_{a0} \exp(-\frac{E_a}{RT})P, \quad v_d = \theta k_{d0} \exp(-\frac{E_d}{RT}). \tag{2}
\]

where \( \theta \) is the surface coverage of the sample, \( k_{a0} \) and \( k_{d0} \) are the coefficients equal to the adsorption and desorption rates at the equilibrium state at \( \theta = 0.5 \), \( E_a \) and \( E_d \) are the energies of the potential barriers of adsorption and desorption, \( R \) is the Mendeleev’s constant, \( T \) is the temperature of the sample surface.

The transition from the rate \( v_a \) to probability of the particle adsorption \( P_{ad} \) at the nanotube surface per time unit is expressed by division of the particle number, deposited per time unit on the emitter surface by number of a free adsorption positions \( (1 - \theta) \). A similar transition takes place for the probability of the particle desorption \( P_{des} \). Thus, probability of adsorption \( P_{ad} \) will depend linearly on the pressure of the residual atmosphere in the chamber \( P \) and exponentially on the surface temperature of the nanotube \( T \). The probability of desorption \( P_{des} \) will also exponentially depend on the temperature, but with a different constant.

To build a computer model we converted the abovementioned formulas to formulas that are simpler and easier to use:

\[
P_{des} = \exp(-\frac{1}{(k_{des})^2}), \tag{3}
\]

\[
P_{ads} = \exp(-\frac{1}{(k_{gas})^2}) \cdot \exp(-\frac{1}{(k_{des})^2}). \tag{4}
\]

where \( k_{des} \), \( k_{ads} \), \( k_{gas} \) are the constants of thermodesorption, thermal adsorption and adsorption from the gas phase respectively, \( P \) is the gas pressure or concentration of the particles in the interelectrode space, \( I \) is the level of the emission current passing through the nanotube, \( T \) characterizes the temperature of the nanotube surface (Joule heat).

In this paper we assumed that the gas concentration in the measuring chamber is constant at a stable emission current level. So we partially neglected the electron-stimulated desorption of the particles from the anode and influence of the vacuum pump. The influence of the electric field, which concentrates at the nanotubes apexes, on the desorption / adsorption probabilities we considered relatively weak too.

The distribution of the emission sites by the heights (that is by the effective field enhancement factors) was specified in the form of a Gaussian distribution with parameters close to the parameters of a real nanocomposite emitters with nanotubes. These parameters are arithmetic average \( a = 1450 \), mean square \( \sigma = 20 \), range \([\beta_{min}; \beta_{max}] = [1300; 1600]\), total number of the emission sites \( N = 350 \), the effective emission area of the one emission site \( S_0 = 1.8 \, \text{nm}^2 \) [13], the work function of electrons from the emission sites without adsorbates of \( \phi_f = 4.6 \, \text{eV} \) [14].

As adsorbate particles the molecules CO were chosen. In [10] the appearance of the CO molecules was registered via mass-spectrometry during the field emission experiment. The attachment of these
particles to the apexes of nanotubes results in a change in its work function by about 0.15 eV [7]. Therefore, we choose the work function to be \( \phi_2 = 4.75 \) eV for the emission sites with adsorbates.

The stochastic change in the work function of the sites during the virtual experiment (adsorption / desorption process) was carried out by method of generating a random number in the range from 0 to 1 and comparing it with the probabilities \( P_{\text{des}} \) and \( P_{\text{ads}} \). Thus in one iteration the nanotubes redistributed between two groups of sites: with adsorbates and without ones.

The probability of the adsorption-desorption process was controlled by a set of parameters \( \{x_{\text{td}}, x_{\text{ad}}, x_{\text{gas}}\} \) which could be changed directly in the course of the virtual experiment to obtain a coincidence of the theoretical and experimental IVCs.

An "infinite" series of triangular pulses with fixed amplitude was applied to the virtual emitter. That resulted in a surface state (distribution of the sites between groups with and without adsorbates) at quasi-stationary mode where the IVC shape changed from pulse to pulse due to the stochastic fluctuations solely. The number of step iterations corresponding to the voltage growth (as well as the voltage drop) in one voltage pulse was equal to 100. This value represents the rate of the applied voltage change, but its influence on the model signals can be replaced by changing of the probabilistic parameters \( \{x_{\text{td}}, x_{\text{ad}}, x_{\text{gas}}\} \).

Figure 1 presents the interface of the program simulating the adsorption-desorption process. Values of the control parameters were chosen arbitrary to produce a reverse type hysteresis in IVC.

![Figure 1. Interface of the program simulating adsorption-desorption process in the field emission system.](image)

The developed program allows not only generates IVC, but also to makes a graph cutting out in order to match the voltage ranges of the virtual experiment to ranges which are available to the experimenter. Then program analyzes this fragment of IVC in semi-logarithmic Fowler-Nordheim coordinates \( Y = \lg(I / U^2) \) and \( X = 1/U \), where \( I \) in amperes and \( U \) in volts, \( Y \) is considered dimensionless). The slope and intercept of the approximation trend line, as well as the field enhancement factor \( \beta \) and the emission area \( S_e \), are calculated for each iteration (the effective work function in these calculations was taken equal to 4.6 eV).

The effective parameters found during the experiment were accumulated and plotted in three diagrams: 1) a point chart of the slope-intercept dependence (the so-called SK-diagram), 2) a histogram of the \( \beta \) values, 3) a graph of the \( S_e(\beta) \) time dependence.
3. Results
As an object of the modeling, we took the field emission cathode based on the nanocomposite carbon nanotubes in polystyrene. Parameters of the experiment: amplitude of a half-sinusoidal voltage pulses $U_{\text{max}} = 1590$ V, amplitude of detected pulses of the emission current of $I_{\text{max}} = 250$ μA, interelectrode distance of $d = 300$ μm.

The change of the values of the parameters $\{x_{\text{ads}}, x_{\text{ads}} - x_{\text{gas}}\}$ made it possible to coincide the shape of the model and experimental IVCs (see Figure 2a). The figure also presents the IVC of the model emitter in two extreme positions: all emission sites without adsorbates (clean), and all with adsorbates (covered).

Fluctuations of the experimental and model IVCs are presented in the "slope-intercept" diagram (see Figure 2b). The similarity of these "clouds" speaks about the mathematical relationship between the results of simulation and online processing of the experiment.

Figure 2c shows histograms of the model and experimental values of the effective field enhancement factor. In works [15] and [16] we studied the movement and change in the shape of this histogram experimentally. It was shown that this histogram is interrelated with the emission current level and level of the vacuum in the measuring chamber.

![Figure 2](image)

**Figure 2.** Experimental and model dependences: a) experimental IVC and IVCs for three states of the model emitter surface, b) slope-intercept diagrams of the IVC fluctuations collected in the real experiment and simulation, c) histograms of the experimental and model fluctuations of the effective field enhancement factor $\beta$, d) effective emission area $S_e$ dependences on $\beta$ for the model and experimental data.
4. Conclusion
The presented model makes it possible to investigate the relation of the experimental method analyzing the IVC fluctuations to the morphology of the field emitter surface and to explain or predict the behavior of the IVC under change in the vacuum conditions. The achieved result is not the final point in the studies and requires continuation of work in this direction. Naturally, the task of achievement a complete coincidence of the observed effects in the multi-tip field emitters IVC with the simulated ones is not solved yet. The real system is much more complicated than any models. Even the well-known Fowler-Nordheim law is just a flat approximation for real multi-tip field emitters and has no direct numerical confirmation for today.

We have developed a methodology for analyzing the emission sites fluctuations of a real multi-tip field emitters using computerized field emission projector. It produces the data about lifetimes of the adsorbates on the nanotubes apexes and allows us to find the effective field enhancement factors of the individual microscopic emission sites.

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