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Application of slope-intercept diagram to determine the parameters of the nanocomposite field emitters in-situ

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Abstract. The method of the field emission data online processing of materials, perspective for a nanoelectronics, is developed. The method is based on the slope-intercept diagram analysis of the current voltage characteristics registered during the experiment. It allows to build calibration grids of the microscopic emission parameters, such as work function, effective emission area and field enhancement factor, and and to estimate changes in the sample structure online.

1. Introduction

Quantum field effects - is one of the essential attributes of modern rapidly developing nanoelectronics. One of such effects is field emission of electrons from multi-tip nanostructures. This type of emitters has already established itself as an energetically favorable and reliable source of electrons. However the combination of accompanying effects doesn't allow it to be used in electronics, requiring careful study of fundamental theory of the process.

Two essential characteristics - stability of emission current and its dependence on the applied voltage appear under the influence of several inaccessible to direct monitoring factors: local Joule heating, adsorption-desorption processes, ion bombardment, influence of ponderomotive forces on the surface morphology, the influence of emitting nanocenters on each other, a nonlinear change in the shape of the potential barrier with an applied voltage, and also charge effects on the emitter surface [1-4].

One of the research methods of the field emitter behavior in various operating modes proposed by leading scientists is the so-called SK-analysis. For carrying out this analysis the current voltage characteristics (IVC) or the series of IVCs in Fowler-Nordheim coordinates (IVC-FN) is built. Then its approximation by straight dependence is made. The obtained parameters of this dependence (slope b and intercept a) are put on SK-chart (this chart is in coordinates "katamuki – seppen", i.e. the "slope – intercept").

The analysis of obtained dependence is a rather complex theoretical problem. The main idea of the method is the creation of a calibration grid, intended for microscopic parameters determination of the emitter during its operation. These parameters are the work function, field enhancement factor (FEF), the average curvature radius of nanotips and the total emission area. However for calculation of calibration "equipotential" lines the detailed data on the parameters mutual dependencies is needed.

The change in the work function with the concentration and the kind of atoms adsorbed on the emitter surface was described by R. Gomer in book "Field emission and field ionization" in 1961 [5]. The increment of work function $\Delta\phi$ was estimated with equation:

$$\Delta\phi = 4\pi N\alpha_p F \tag{1}$$

where N is the adatom concentration, α_p – coefficient of the adatom polarization, F - local electric field. By the way it was claimed that electronegative adatoms on the emitter surface act like a barrier which repulses electrons, due to which total emission current decreases, and positive ones act like a window in the potential barrier, due to which the current increases.

The introduction of the dependence from eq. (1) to the standard Fowler-Nordheim equation and the decomposition of subexponential expression in Taylor series for small increment $\Delta\phi$, allowed to obtain a multiplier for emission area correction. So the real area S_0 must be different from the estimated area S_e (calculated without taking into account sorption amendment):

$$S_e = S_0 \exp(-9{,}74\cdot 10^7 \cdot \gamma \cdot \sqrt{\phi}) \tag{2}$$

where $\gamma = 4\pi N\alpha_P$, coefficient α is connected with deviation of the potential barrier shape from a triangular one under the influence of image forces (Nordheim, 1928).

In 1976 Spindt used this theory to explain fluctuations of the emission current from molybdenum tip and the moving of the emitting centers in the field emission projector picture [6]. Coefficient α was accepted equal to 0,95. The same value was used subsequently by other scientists.

In 1993 the Japanese scientists Gotoh, Ishikawa and Tsuji first tried to build a calibration grid for SK-chart on the basis of Fowler-Nordheim equation without sorption correction [7]. The assessment of the golden microtip work function using this grid showed doubtful results, so it was decided to use an correction from eq.(1). However at the same time in the multiplier for emission area correction was included one more factor – field enhancement factor β:

$$\gamma' = 4\pi N\alpha_p \cdot \beta \tag{3}$$

To determine unknown parameters – S_0 (emission area without adatoms) and γ (proportionality factor $\Delta\phi$ and F from eq.(1)) the equations of slope and intercept of IVC-FN were used:

$$a = \log\left(1{,}4\cdot 10^{-6}\cdot S_e \cdot \frac{\beta^2}{\phi}\right) + \frac{4{,}26}{\sqrt{\phi}} \qquad b = -2{,}82\cdot 10^7 \cdot \frac{\phi^{3/2}}{\beta} \tag{4}$$

The resulting dependence was fitted for the golden tip experimental data (ϕ = 5 eV), so that the parameters were equal to: $S_e = 10^{-8}$ cm^2, $\gamma = 10^{-13}$. For this time the experimental data for other materials (nickel, molybdenum and chromium), according to the calibration grid on SK-chart, showed plausible results.

In 1996 the same group of scientists used eq.(2) again for creation of the calibration grid according to the field emission experimental data of tungsten wire with nickel coating [8]. This time they thoroughly showed that the decrease/increase in work function leads to a shift of IVC-FN parameters in SK-chart to the right-upwards/left-down, and decrease/increase of the emitting tip radius – to the left-up/right-down shift.

In 2004 Gotoh et. al. considered the influence of aging in atmosphere of oxygen, hydrogen and carbon dioxide on emission of platinum microtip [9]. In the field emission projector pictures wandering spots were observed. The authors explained its by the adsorption and desorption of individual atoms in different regions of the tip. It was shown that the exposure of the emitter in hydrogen reduces emission current (at the same time the relative flicker noise is reducing), and in oxygen- reduces it even more. Aging in carbon dioxide, on the contrary, increases current level (in this case the noise increased).

SK-chart of IVC noise dependence showed a linear relationship between slope and intercept:

$$b = a \cdot A_c + B_c \tag{5}$$

The observed line was perpendicular to the line of work function change on calibration grid, which allowed to assert that the noise fluctuations are due to a change in FEF. Mathematical analysis of this linear connection indicates that all of noise IVC-FN must converge in one point with coordinates $1/V=-A_c$ and $lg(I/V^2)=-B_c/A_c$.

The application of SK-analysis to arrays of nanotubes (thickness of 10 nm, grown on ITO coating) allowed the scientists from South Korea to evaluate the change of microscopic parameters of the emitter after its operation in the modes of constant (DC) and alternating (AC) voltage [10].

The Chinese scientists also used SK-chart for analyzing of the change of multi-tip emitter made of nanotubes grown by CVD method on a silicon substrate [11]. There was observed a drop in FEF from 5000 to 2000, which the authors associated with the longest burnout of nanotubes under ion bombardment of oxygen atoms.

In 2013 an American scientist A. Persaud simulated a noise dependence of IVC-FN on SK-chart through the introduction of the specified distribution of virtual nanocenters for height, radii, and work function [12]. He showed that the bias of stochastic cloud on SK-chart to the left and down can be caused not only by the change of the work function, but also of the number of emitting nanocenters.

In 2014 we used his assumption of normality of the nanocenters distribution in the nanocomposite emitter (nanotubes in the dielectric polymer matrix) to analyze the dependence of nanocenter distribution by the effective heights from the level of applied voltage [13].

2. Expriment

The experimental installation for the study of the field emitter emission characteristics is described by us in detail in [14]. The installation is computerized and allows to process the registered IVCs and to obtain the microscopic parameters of the emitter online (data processing program was created with the LabView platform). IVCs are registered in a "fast" mode with frequency of 50 Hz by scanning with the half sine pulses. The vacuum in the chamber is maintained at 10^{-7} Torr. The distance between the electrodes d in this work was equal to 300 μm. The sample area S_k was 0,79 cm^2.

The sample for the study was a nanocomposite emitter fabricated on the base of graphene and polystyrene. The substrate was a circular plate of stainless steel. Over it by means of the rotating table was applied the suspension: graphene with polystyrene in the ratio of 1/10 in the organic solvent orthoxylol. For reduction of the size of nanotubes agglomerates and better dissolution of polymer, the suspension before the application was treated in an ultrasound bath for several hours.

Online analysis of the recorded IVCs uses the standard field emission equation in approximation of Elinson [15], written in the coordinates of Fowler Nordheim:

$$\lg\frac{j}{E_0^{\,2}} = \lg\left(A_\phi\right) + B_\phi\cdot\frac{1}{E_0} \tag{6}$$

where j is the emission current density, E_0 is the electric field on peaks of the emitter tips, A and B are the coefficients that depend on ϕ - emitter work function (the influence of adatoms on emission current will be incorporated in S_e):

$$A_\phi = \frac{1{,}4\cdot10^{-6}}{\phi}\cdot10^{4{,}39/\sqrt{\phi}} \tag{7}$$

$$B_\phi = -2{,}82\cdot10^{7}\cdot\phi^{3/2} \tag{8}$$

Expressing the microscopic quantities E_0 and j through the macroscopic analogues we can get:

$$\lg\frac{J}{E^2} = \lg\left(\frac{\beta^{2\cdot}\cdot A_\phi\cdot S_e}{S_k}\right) + \frac{B_\phi}{\beta}\cdot\frac{1}{E} = a + \frac{b}{E} \tag{9}$$

where J - the macroscopic current density: $J = I / S_k = j\cdot S_e / S_k$,

E - macroscopic field : $E = E_0 / \beta = U / d$.

The linear approximation of the experimental data plotted in the same coordinates allows us to find the slope b and the intercept a (see Fig.1a,b). The linear dependence of b on a can be analyzed online by obtaining the corresponding coefficients A_C and B_C (see eq.(5)).

During the operation of the emitter its IVC demonstrates a flicker noise, so that slope and intercept of the corresponding approximation have some variations. Received in just a few seconds of the emitter work b-set and a-set were deposited on the SK-chart (see Fig.1c,d).

The coefficients b and a are connected with the parameters S_e, β and ϕ (see eq.(9)):

$$a = \lg\left(\frac{\beta^{2\cdot}\cdot A_\phi\cdot S_e}{S_k}\right) \qquad b = \frac{B_\phi}{\beta} \tag{10}$$

The signal processing program calculates the parameters β и S_e from the experimental a and b automatically (work function ϕ in this calculation is set by the experimenter).

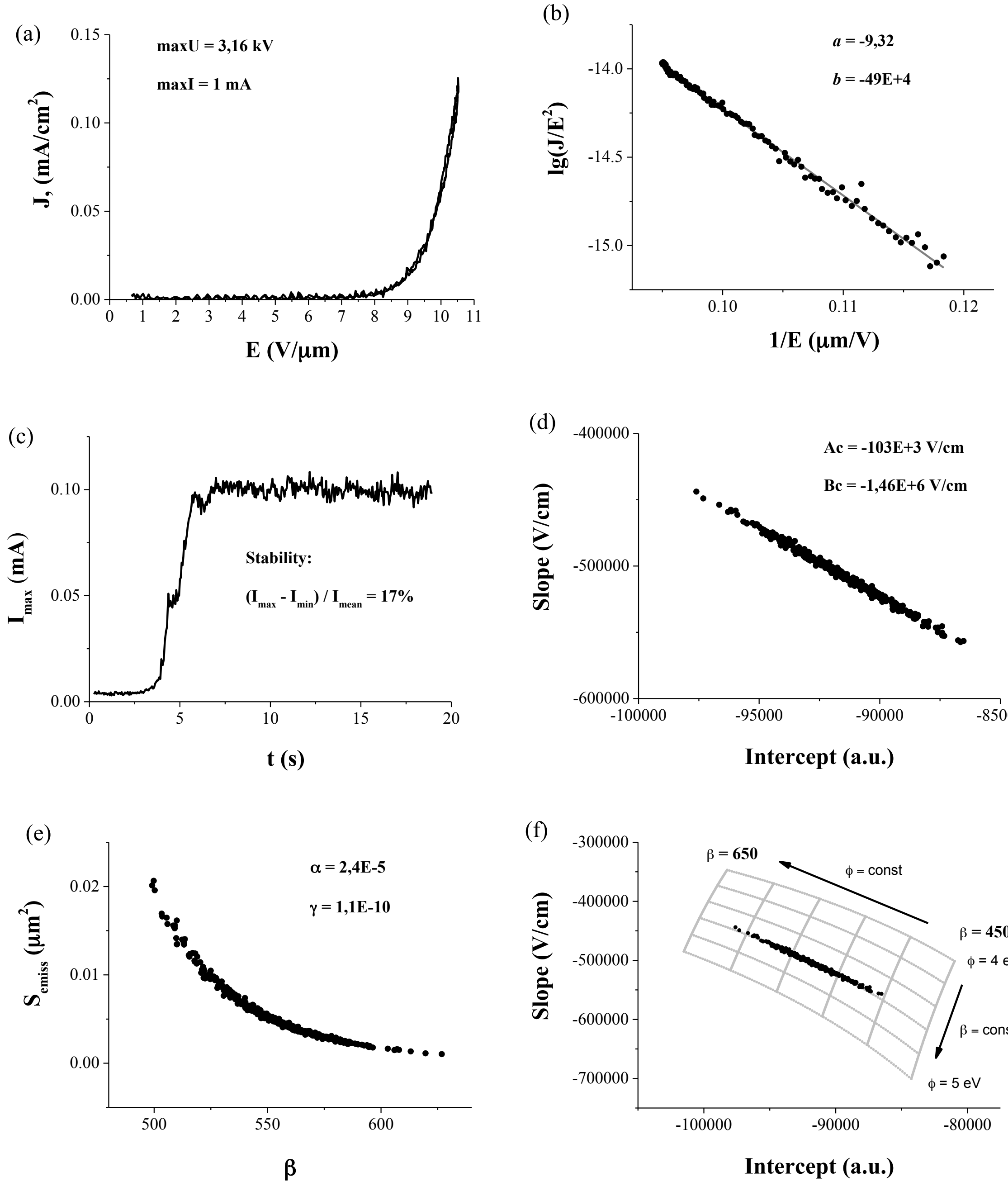

Figure1. The examples of the dependences obtained during field emission experiment with graphene nanocomposite: a) IVC in macroscopic coordinates J and E, b) corresponding IVC-FN, c) noise dependence of amplitude of the emission current pulses from the time in a stable emission mode, d) SK-chart of IVC-FNs obtained for the shown period of time, e) dependence of emission area S_e from the FEF β, calculated for the presented chart, f) calibration grid in the SK-chart which is built with derived coefficients α_0 and γ.

Figure 1e shows the dependence of S_e on β which is obtained by processing noise data from the «cloud» presented in Figure1d. Its exponential shape allows us to apply the approximation in agreement with the dependences in eq.(2) and eq.(3). As a result of approximation of the noise data, adsorption coefficients α_0 and γ are obtained. With the help of these coefficients a separate software module calculates calibration grid and puts it on the experimental SK-chart of the current IVC-FN (see Figure1f).

When the applied voltage amplitude rises the point in the SK-chart, corresponding to the actual IVC-FN, moves across the grid lines. But if the amplitude does not change the noise «cloud» in the SK-chart has almost linear form and seems tangentially to the equipotential line of the grid with corresponding work function ϕ. This fact indicates basic distinction of two processes: fluctuation change of current at the constant level of voltage (U = const) and the change of current due to the change of applied voltage amplitude of ($U \neq$ const).

The first process is obviously connected with wanderings of the emitting areas on the sample surface (we observed this effect in the work [16]). Many authors connect these wanderings with stochastics of the adsorption processes. The second process cardinally changes a condition of fluctuation balance, leading to a change of conditions of nanocenters mutual influence and the speed of adsoption-desorption processes.

Further studying of fundamental dependences in the field emission processes of multi-tip emitters with application of SK-analysis will be continued by us with using computerized field emission projector and also with statistical modeling of multi-tip emission systems.

3. Conclusion

We developed a method for online analysis of SK-charts of the large area field emitters. The calibration grid constructed on the noise dependence of the calculated emission area from the effective FEF, allow to analyze changes in the microscopic parameters of the emitter while changing the scanning voltage amplitude. We consider that the linearity of the noise dependence in the SK-chart at a constant voltage level is due to balancing of the microscopic emitter parameters near the equilibrium point. Correlation of this line with the equipotential curves of the calibration grid requires further research including not only derivation of empirical dependences, but also a modeling of field emission in stochastic multi-tip system.

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