Operating voltage diminution of field emission cathodes based on carbon nanotubes

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Abstract. The possibility of minimizing the operating voltages of the diode structure with a field emission cathode based on an array of carbon nanotubes is investigated. The numerical simulation method was used to perform theoretical calculations that showed the potential for an unlimited reduction in the operating voltage by reducing the diameter of the emitters, increasing the height of the emitters and reducing the value of the interelectrode gap. Established deviation of the experimental values of the operating voltage from theoretically calculated when approaching in the interelectrode gap near to values commensurate with the height of the emitters. It is shown that the observed effect is caused by low conductivity of multi-walled carbon nanotubes, high contact resistance with a substrate, as well as micro- and macroinhomogeneities of the structure of an array of carbon nanotubes.

1. Introduction

One of the promising and intensively studied fields of carbon nanotubes (CNTs) application is field-emission cathodes (FECs) [1]. FECs can be used in a series of devices, such as compact high-frequency electron sources, powerful microwave amplifiers, compact X-ray sources, sources of synchrotron radiation, high brightness flat-panel displays, high-performance luminescent lamps etc. The attractiveness of CNTs for these applications is due to their electrical, chemical, thermal and mechanical properties, that are reached owing to quasi one-dimensional structure and naturally high aspect ratio. Regardless of the field of FECs application, a number of requirements to their characteristics must be satisfied. Among them are the high emission efficiency, high homogeneity, density and stability of electron emission. Of particular interest is the field of vacuum integrated micro- and nanoelectronics – a new class of miniature vacuum electronic devices and vacuum integrated circuits based on CNT FEC [2]. These new devices have an ultra-high speed (subpicosecond), high radiation resistance, low sensitivity to temperature and a large coefficient of efficiency.

One of the key problems of vacuum integrated micro- and nanoelectronics is the problem of minimizing the operating voltage at a fixed value of the field emission current. It is associated with the limited values of the breakdown voltages of dielectrics used in microelectronics and the relatively small values of their working thicknesses. According to the existing theoretical ideas, there are no reasons preventing the reduction of operating voltages CNT FEC to arbitrarily small values by optimizing the geometry of the cathodes. In particular, an increase in the emitter amplification factor, a
decrease in the diameter of the emitter and the interelectrode gap of the anode-cathode should lead to a decrease in the operating voltage to an arbitrarily small value. However, the results of experimental studies indicate that there is an effect limiting the possibility of minimizing the operating voltage of CNT FEC.

2. Experimental

The arrays of CNTs were synthesized by CVD method realized by a high temperature pyrolysis of fluid hydrocarbon ($p$-xylene [C$_8$H$_{10}$]) mixed with the volatile source of catalyst (ferrocene [Fe(C$_5$H$_5$)$_2$]) using pre-structured localized catalyst on the $n$-type silicon wafers with high doping level KES-0, 01 (100) of the size of 5×5 mm$^2$. The content of ferrocene in this “feeding solution” was 0,1% wt %. Process was conducted under the atmospheric pressure by using Ar as a gas-carrier. The aerosol of the feeding solution is delivered into the synthesis zone by dosed injection at a rate of $0.15 \div 0.5$ cm$^3 \cdot$min$^{-1}$, a speed of the flow of Ar was $100$ cm$^3 \cdot$min$^{-1}$. The synthesis process was realized in the tubular type quartz reactor of the specially constructed equipment at relatively low working temperature of 650 °C and synthesis time of $t = 4$ minutes. The speed of the cooling was determined by the process of natural cooling of reactor.

The localized catalyst is a metallic layer of Al\Ni with thickness of 10 nm and 1 nm, respectively. To prevent interaction of Al with Si the Si-substrate was coated with molybdenum film of 200 nm thickness. The topology of the test structure is obtained by lift-off photolithography.

As it is shown in our patent [3], the use of volatile catalyst Fe from (C$_5$H$_5$)$_2$Fe source in combination with the multilayer localized catalyst Mo\Al\Ni, playing role of the activator of metal-organic compound dissociation, insures obtaining the few-wall CNTs with narrow diameter distribution of low defect density, high adhesion to the substrate and minimum micro- and macro nonuniformity of CNTs height.

Study of the geometric features of the experimental samples of CNT FECs were carried out using a scanning (JEOL 6510) and transmission (JEOL 100CX) electron microscopes. The field emission (FE) properties of the experimental samples of CNT cathodes were investigated in DC mode using a diode-type cell with a fixed spacer (BSUIR).

The matrix structure of CNT PEC of densely packed single elements with a 5 μm step is shown in figure 1 (a, b) (SEM). The internal structure of carbon nanotubes is shown in figure 1 (c) (transmission electron microscopy, TEM). We can see a carbon nanotubes with $5 \div 10$ nm in diameter.

![Figure 1. Microphotographs (a, b) of scanning electron microscopy of an array of carbon nanotubes; (c) a micrograph of the internal structure of carbon nanotubes (transmission electron microscopy).](image-url)
3. Results and discussion

3.1 The relationship of the operating voltage and the interelectrode gap CNT FEC

The field emission current of the emitter on the basis of a single carbon nanotube is determined by the value of the local electric field intensity $E_{FE}$ at its vertex in accordance with the classical Fowler-Nordheim formula [4-6]:

$$ I_{FE} = \frac{A S E_0^2}{\varphi} \exp \left[ -\frac{B \varphi^{3/2}}{E_0} \right] \text{A/cm}^2, $$ (1)

where $E_0$ – local electric field intensity at the emitter tip (V/cm), $S$ – emission area (cm$^2$), $\varphi$ – work function for emitter material (eV), $A = 154$ and $B = 6830$ – constant values. For multi-walled carbon CNT $\varphi = 5$ eV [7, 8]. In its turn $E_0 = \beta \cdot E_{FE}$ – where $E_{FE}$ – the intensity of the electric field in the gap between the tip of the emitter and the anode, $\beta$ – field amplification factor.

The fixed current value uniquely corresponds to a fixed local electric field intensity $E_0$ at the vertex of emitter. Then, the operating voltage $U_{FE}$ at the interelectrode gap cathode-anode required to create such an autoemission current will be determined by expression:

$$ U_{FE} = \frac{E_0 (L-h)}{\beta} $$ (2)

where $E_0$ – local electric field intensity at the vertex of emitter, $L$ – interelectrode gap between cathode and diode cell anode, $\beta$ - field amplification factor near the tip of the emitter, $h$ – emitter height.

We use the expression for the coupling of the amplification factor $\beta$ and geometric parameters of the emitter on the basis of a single carbon nanotube:

$$ \beta = \frac{h (1 + \frac{d}{L-h})}{d} $$ (3)

where $h$ and $d$ are respectively, the height and diameter of the nanotube, $L$ – cathode-anode interelectrode gap.

As a consequence, we obtain the dependence of the operating voltage $U_{FE}$ from geometric parameters $h$, $d$ and $L$ diode cell cathode-anode with a single nanotube at a fixed value of the field emission current:

$$ U_{FE}(h, d, L) = \frac{E_0 h d}{h (1 + \frac{d}{L-h})} $$ (4)

A practical variant of the field emission cathode based on carbon nanotubes is the array of carbon nanotubes, formed on the surface of a functional substrate in the CVD synthesis. A feature of this array is a large spread of geometric parameters of carbon nanotubes in height and diameter, and the stochastic distribution of carbon emitters over the substrate surface. As a consequence, in the case of an array of carbon nanotubes as additional descriptive parameters a distance parameter appears between the individual nanotubes in the array and the parameters, characterizing the dispersion (variance) of the values of individual parameters of CNT in terms of diameter, height and distance between them.

The formula (4) allows to estimate qualitatively the character of dependence $U_{FE} = f(h,d,L)$. More detailed modeling of the dependence $U_{FE} = f(h,d,L)$ for an array of carbon nanotubes requires taking into account the effect of electron tunneling through a potential barrier near the surface of a solid in a vacuum. We carried out this simulation on the basis of a numerical solution of the Poisson equations together with the quantum-wave equation in the one-electron approximation. The calculation procedure is outlined in the work [9]. The dependences of the working voltage of the diode structure based on CNT FECs on the cathode-anode interelectrode gap at a fixed emission current density and variations in the diameter and height of carbon emitters are calculated. For each set of variables $h$, $d$ and $L$ an optimization was performed on the distance between the emitters in the array and the minimum value of the operating voltage. It was find out that the characteristic qualitative form of the obtained dependences $U_{FE} = f(h,d,D)$ practically does not depend on the density of the emission.
current. The results of calculations for a fixed emission current density of 1 A/cm$^2$ are shown in figure 2. As we can see, theoretical calculations by the numerical simulation testify to the potential for an unlimited reduction in the operating voltage due to a decrease in the emitter diameter, an increase in the emitter height, and a decrease in the interelectrode gap.

To verify theoretical calculations, we fabricated diode structures with FECs based on arrays of carbon nanotubes and investigated the dependence of the operating voltage on the value of the interelectrode gap $L$ cathode-anode for three heights of CNT – $h = 2, 5$ and $10$ μm. The CNT FECs and the internal structure of synthesized emitters are shown in figure 1 (a-c).

The current-voltage characteristic of the diode structure was measured in DC mode. On the basis of the measured current-voltage characteristics, the dependence of the operating voltage on the value of the interelectrode gap is constructed for a fixed value of the emission current density of 1 mA/cm$^2$ (figure 3).

The dashed lines in figure 3 show the course of the theoretically calculated dependences $U_{FE} = f(L)$ at fixed values $d$ and $h$. Theoretically calculated dependences are combined with those obtained by experimental measurements of the current-voltage characteristics. As we see, with a decrease in the interelectrode gap of the cathode anode to values commensurate with the height of the emitters, the deviation of the experimental curves $U_{FE} = f(L)$ from theoretically calculated is observed. Namely, with a decrease in the interelectrode gap in the experimental diode structure, the decrease in the operating voltage for a fixed value of the field emission current is rapidly slowed down.

The registered effect is the main obstacle for the use of CNT arrays as field-emission cathodes in the field of a new perspective direction of work - vacuum micro- and nanoelectronics, since it does not allow to perform the required micro- and nano-miniaturization of field emission cathodes. In this regard, relevant work is to explain and search for possible causes of the observed effect.
3.2 Minimum operating voltage limiting mechanism of CNT FEC

There are reasons to believe that three known facts can be related to the underlying causes of the observed effect – low conductivity of multi-walled carbon nanotubes, high contact resistance with a substrate, as well as micro- and macroinhomogeneities of the structure of the CNT array.

In practice, the individual emitters, as a rule, are multi-walled CNTs. They are characterized by a significant defect structure of graphene walls, causing a low electrical conductivity of CNTs. Another problem is poor mechanical, electrical and thermal contact with the substrate. As follows from [10], the conductivity of multiwall CNTs in practice corresponds to the conductivity of graphite, therefore the resistance value of the CNT array is of the order of several megoOhms. Moreover, one should keep in mind that due to the significant dispersion of CNTs geometric parameters in the cathode (height, diameter and distance) the main contribution to the emission current yield gives at best a few percent of the CNTs. Taking into account all this together the actual resistance of the CNT emitters can reach hundreds of megoOhms.

Further, a decrease in the interelectrode gap leads to a proportional decrease in its resistance, whereas the emitter resistance and a contact resistance of emitter-substrate is constant. This situation leads to the fact that, beginning from the certain values of the interelectrode gap only some part of the applied potential falls on the discharge gap, and a significant part of the potential falls on the high resistance emitting nanotubes and their contact with the cathode substrate. As a consequence, higher operating voltages are required to maintain a fixed density of the emission current in the diode cell. Beginning with some gap size, almost all of the operating voltage applied to the electrodes of the diode structure falls on the carbon nanotubes and their contact with the cathode substrate. Thus, the minimum possible value of the operating voltage CNT FEC is determined by the resistance of the carbon emitters and their contact with the cathode substrate. It should be noted that this same mechanism underlies another known effect – the so-called emission current saturation effect [11]. This effect is manifested in the pronounced inflection of the current-voltage characteristics and Fowler-Nordheim dependences at a sufficiently large emission current densities [12].

Another reason for the observed effect of limiting the minimum operating intensity of CNT FEC may be a statistical spread of the structural parameters of individual emitters over the area of the CNT cathode, associated with the imperfection of the CVD technology of CNT synthesis. In the case of a cathode with a significant number of point emitters, an ideal homogeneity (uniformity) of the structure along the height and diameter of the individual emitters, the distance between them, and the interelectrode gap value is required. In practice, the ideal unification of the structure of CNT in processes of self-organization (growth) is technologically difficult to achieve in all known growth technologies, such as CVD, arc discharge, laser ablation, etc. In all mechanisms of synthesis, it is impossible to avoid heterogeneity in diameter, height of carbon nanotubes, and the distance between them.

As already mentioned, the emission current $I_{FE}$ of field-emission cathodes is described by the modified Fowler-Nordheim expression (1). In accordance with the Fowler-Nordheim formula, as well as its generalization for thermofield emission, the Murphy-Hood formula [13], the values $I_{FE}$ and $E_0$ are related by an exponential dependence. In accordance with the formula (2) the same exponential relationship exists between $I_{FE}$ and $U_{FE}$. Depending on the CVC area, the increment $U_{FE}$ at 10% may lead to an increase of $I_{FE}$ of an individual emitter in $5 \div 10$ times. On the other hand, the statistical variation in height and diameter of individual emitters can significantly affect $U_{FE}$, since the height of the emitter determines the interelectrode gap between the emitter and the anode, and the emitter diameter is the internal field amplification factor $\beta$ on an individual emitter. The interrelationships of $U_{FE}$ with $h$, $d$ and $L$ follow from the formula (4).

The statistical spread of the geometric parameters of neighboring tip emitters (individual carbon nanotubes) can be defined as microinhomogeneities of the structure. At the same time, also the heterogeneity of the CNT parameters at different parts of the cathode matrix begins to play a role on a large working area of the cathode, determined by the inhomogeneity of the growth conditions of CNT on the extended synthesis zone in the CVD reactor. Such heterogeneity can be defined as
macroinhomogeneity. In the process of CVD synthesis, the microinhomogeneity of the array structure (the spread of the geometric parameters of neighboring CNTs in the array), as a rule is 5% - 10% from average values of height and diameter of CNT. With a decrease in the interelectrode gap, an increasing proportion of CNT with a lower coefficient of amplification of the electric field (small height and large diameters) are excluded from effective emission, since due to the exponential nature of the dependence \( I_{FE} \) on \( U_{FE} \) their emission currents drop sharply. A similar contribution is made by the macroinhomogeneity of the CNT array, determined by the heterogeneity of the growth conditions of CNT in the extended zone of synthesis of the CVD reactor. The effect is manifested in a decrease in the area of effective emission relative to the cathode working area. A decrease in the area of effective emission leads to a reduction in the total emission current. As a consequence, the preservation of the value of the emission current stationary requires higher operating voltages at the electrode gap cathode-anode, which compensates for the decrease in the area of effective emission. Negative result is overload, burning out of the most active emitters and destruction of the cathode.

Thus, the low conductivity of multi-walled carbon nanotubes, the high contact resistance with the substrate, and the micro- and macroinhomogeneities of the structure of the CNT array are the main reason for limiting the minimum operating voltage of the diode cell with CNT FEC.

4. Conclusions
The possibility of minimizing the operating voltages of field emission cathodes on the basis of arrays of carbon nanotubes is investigated. Theoretical calculations are performed by the numerical simulation method, which showed the possibility of an unlimited reduction in the operating voltage of CNT FECs by reducing the diameter of the emitter, increasing the emitter height and reducing the value of the interelectrode gap.

To test the theoretical calculations, studies of the dependence of the operating voltage CNT FECs on the value of the interelectrode gap \( L \) cathode-anode for three heights CNT - \( h = 2, 5 \) and 10 \( \mu \)m were carried out. CVC were measured in a diode structure in an DC voltage mode.

It is shown that when the cathode-anode inter-electrode gap is reduced to values commensurate with the height of the emitters, the deviation of the experimental curves \( U_{FE} = f(L) \) from theoretically calculated is observed. In practice, with a decrease in the interelectrode gap, the decrease in the operating voltage for a fixed value of the autoemission current is rapidly slowed down.

It is shown that the observed effect is caused by low conductivity of multi-walled carbon nanotubes, high contact resistance with substrate, as well as micro- and macroinhomogeneities of the CNT array structure.

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