INTERRELATION OF PLANCK THERMAL GLOW WITH CURRENT SATURATION EFFECT OF CARBON NANOTUBE FIELD EMITTERS

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The interrelation of the emission current saturation effect with Planck glow in the visible spectral range of the matrix field emission carbon nanotube based cathodes was investigated. It was found that the beginning of the glow in the visible spectral range corresponds to the beginning of the transition into the emission current saturation mode. It was found that the main reason for the emission current saturation is high internal resistance of carbon nanotubes and its contact with substrate.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, continuous research of them reveals more and more unique properties and new areas of application [1]. One of the promising and intensively studied fields of CNT application is field-emission cathodes (FECs). FECs can be used in a series of devices, such as high brightness flat-panel displays, compact X-ray sources, powerful microwave amplifiers, high-performance luminescent lamps, compact high-frequency electron sources, sources of synchrotron radiation 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, low threshold and operating voltages, high homogeneity, density and stability of electron emission.

The theoretical limit of the current density of field emission cathodes based on CNT reaches 10^9 A/cm^2 [2]. For a number of important applications, particularly in the field of vacuum microwave electronics (transistors, klystrons, traveling wave tubes) required current density is more than $1 \div 10$ A/cm^2 [3]. However, until recently the practical implementation of such cathodes is problematic. One of the reasons is the so-called emission current saturation effect [4]. This effect is manifested in the pronounced inflection, of the current-voltage characteristics and Fowler-Nordheim dependences at a sufficiently large emission current densities.

A number of attempts to explain the origin of the saturation effect were taken. In [5] this effect was associated with the field amplification factor β, in the papers [6,7] - with the presence of adsorbents at the CNTs apex. Authors of articles [4,8] demonstrated that it is due to a large voltage drop along the CNT emitter and emitter/substrate contact. Due to the complex nature of the field emission processes other explanations may be attracted. For example, in the case of silicon emitters the change of current-voltage characteristics slope and Fowler-Nordheim dependence have been attributed to the problem of the potential supply to the emitting part of FEC through a complex chain comprising silicon substrate, metal underlayer, carbon tubes and contact layers including semiconductor junctions and Schottky barriers creation in the chain of FEC feeding [9].

In the present paper we propose the mechanism of emission current saturation by attracting well known experimental effect – the appearance of glow in the visible spectral range in the area of the field emission at sufficiently large emission current densities. The appearance of glow in CNT FECs have been noted by the authors of a number of articles [10,11,12], but its nature is still a controversial issue. In [11] the glow associated with the phenomenon of fluorescence, in [12] - with the effect of the filament, but without any proof. In [10], based on the results of emitted electrons energy distribution studies, it was shown that in the process of multi-walled CNTs emission the emitters can be heated up to 2000 K and above without substantial loss of emission properties. There has also been supposed that glow in the CNT FECs may be related to the thermo- heating (Plancks thermal radiation). In the case of sufficiently large current densities the temperature of emitters can be raised up to the temperature of the carbon material decomposition (4500 - 5000 K) [13]. It was shown by simulation [14, 15] that at such temperatures there is a probability of transition from field electron emission to the thermo-field emission. However, as it is noted by the authors [15], due to the considerable uncertainty of available data on the temperature dependences of transport coefficients for carbon nanotubes,

it is not possible to construct by modeling the current-voltage characteristics of CNT FEC at high operating temperatures and high densities of the emission current. At the same time, in practice, just at these conditions a glow effect reveals under emissions, leading to the CNT FEC current saturation effect.

Thus, the experimental study of the relationship of the emission current saturation effect of the matrix CNT FEC with Planck glow of the emission area in the visible spectral range represents the doubtless interest. Such studies may provide useful information on the specificity of current saturation effect mechanism and the possibility to eliminate this effect and create as a result the CNT FECs with high density of the emission current (up to tens of A/cm^2 and more) that is required for the high frequency vacuum microelectronics.

2. Experimental

The arrays of CNTs were synthesized by CVD method realized by a high temperature pyrolysis of fluid hydrocarbon (*p*-xylene [C_8H_{10}]) mixed with the volatile source of catalyst (ferrocene [$Fe(C_5H_5)_2$]) 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 - 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 [16], the use of volatile catalyst Fe from $(C_5H_5)_2Fe$ 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 (2-6 walls) 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 FECs were investigated with the field emission scanning microscope (FESM) (Wuppertal University, Germany) at a residual gases pressure of 10^{-9} Torr. in cyclic measurement mode (multiple raising and dropping of the operating voltage). High-resolution video-camera built into the vacuum chamber, allowed to observe the emission region in real time.

SEM images of the matrix FECs emitting elements are presented in Fig.1. The topology of emitting elements represents a set of simple elements of 2×4 μm^2 with 5 μm spacing. Active area of the samples is 0,25×0,5 mm^2 with an overall chip size of 1,2×3 mm^2.

Fig. 2 shows the current-voltage characteristics (CVC) and Fowler-Nordheim dependences of the CNT FEC samples in cyclic measurement mode. Voltage sweep rate - 5 V/s. CVC is measured to a value of the emission current $8 \cdot 10^{-4}$ A, which corresponds to the emission current density of 0.64 A/cm^2 from

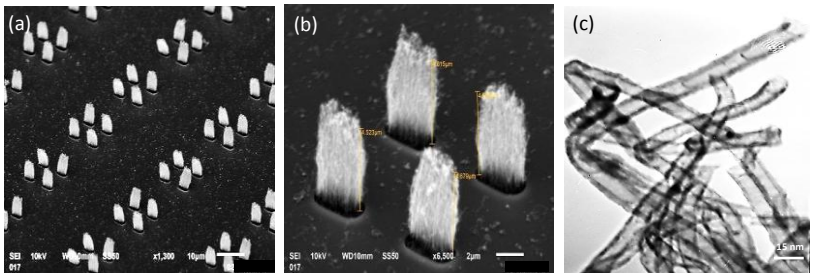

Fig. 1 – SEM images of the matrix FECs emitting elements
a, b - scanning electron microscopy; c – transmission electron microscopy

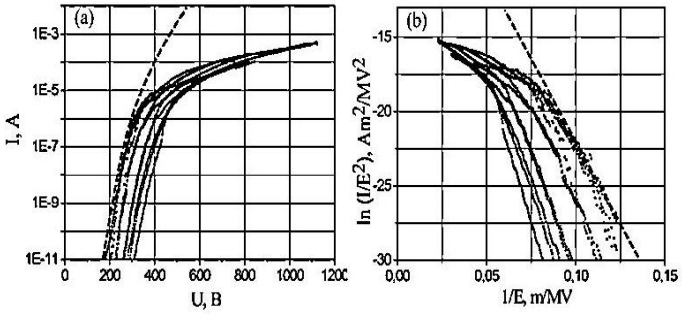

Fig. 2. The current-voltage (a) and according Fowler-Nordheim (b) characteristics for CNT FEC sample with emission work area 0,25 ÷ 0,5 mm^2, obtained by the cyclic measurements.

cathode area $1{,}25 \cdot 10^{-3}$ cm^2 suitable for CNT FEC practical use. These parameters correspond to the level of the best published results on CNT FEC.

As can be seen from the curves, cyclic loading leads to a shift of the emission threshold voltages towards higher values (from 170 V to 310 V), what may be associated with the processes of CNT emitters degradation at large emission current densities. Fig. 2 shows (dashed line) the theoretically expected Fowler-Nordheim dependences according to the Fowler- Nordheim equation. But starting from the current values $10^{-6} \div 10^{-5}$ A the deviation of the experimental curves from the theoretical to the lower current values takes place (so-called "emission current saturation effect").

Fig. 3 shows photomicrographs of the emission area of the same sample at different values of the emission current in the process of CVC measurement within the first cycle of measurements. As one can see the separate glowing centers in the emission area appear at the emission current value of 10^{-5} A (Fig. 3a), what correlates with the appearing of the saturation effect of emission current on the current-voltage characteristics and the Fowler-Nordheim dependences (Fig. 2ab). Nonhomogeneity of the glow along the emitting area is determined by the variation of geometrical parameters of the carbon nanotubes (height, diameter, distance).

With the increasing voltage on electrodes the number, size and brightness of the emission centers increases, but the localization of the centers remains unchanged what is clearly seeing from Fig. 3b ($I = 1{,}5 \cdot 10^{-5}$ A) and Fig. 3c ($I = 4{,}0 \cdot 10^{-5}$ A).

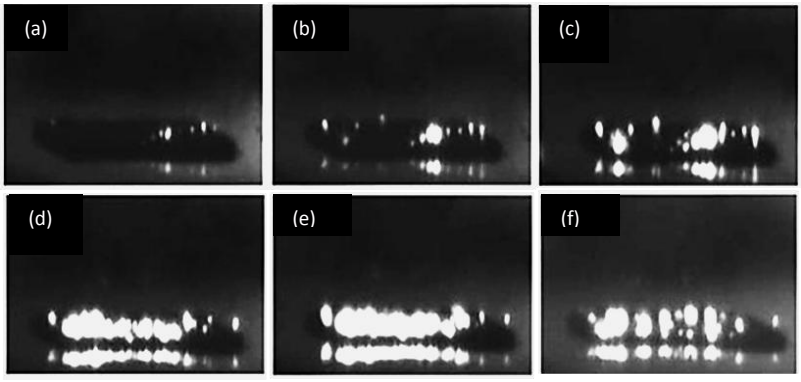

Fig. 3. The micrographs of the CNT FEC emission area at different values of emission current: glow in the process of changing emissions from the rise of the working voltage. Emission work area (dark) - 0,25 ÷ 0,5 mm^2: a) $I = 10^{-5}$ A; b) $I = 1{,}5 \cdot 10^{-5}$ A; c) $I = 4{,}0 \cdot 10^{-5}$ A; d) $I = 10^{-4}$ A; e) $I = 5{,}4 \cdot 10^{-4}$ A; f) current failure to $I = 4{,}8 \cdot 10^{-4}$ A.

With the further growth of the emission current the glowing centers conjugate into the continuous area of the glowing surface what is retained up to the top point on the CVC ($8 \cdot 10^{-4}$ A), which corresponds to Fig. 3e. With the further voltage increasing the emission current decreases sharply up to the value of $I = 4{,}8 \cdot 10^{-4}$ A what indicates on the beginning of the process of overloaded emitters destruction (Fig.3f). Thus, the experimental value of the emission current is many orders of magnitude smaller in the tested samples then theoretically expected values, which is shown by a dotted line in Fig. 2ab.

3. Results and discussion

As it was already mentioned, many authors in a number of papers have tried to explain the origin of the emission current saturation effect [4-8]. One of the approaches is following. As it is known, the slope angle ($\mathrm{tg}\alpha$) in the F-N coordinates is proportional to the ratio of the material work function φ and the electric field enhancement factor β ($\mathrm{tg}\alpha \approx \varphi/\beta$). The work function depends on the sorption-desorption processes of the residual gases on the emitter apex, and the emitter temperature [14], while the electric field enhancement factor β is mainly determined by the geometric parameters (say, aspect ratio) of the emitter. In [5] the effect of emitter current saturation is attributed to the change of the field enhancement factor β. The authors of [6, 7] believe that the reason – in the presence of adsorbates (adsorbed molecules or impurities) at the CNT apex. Another hypothesis is [8] that the presence of a resistance in series with the emitter can induce a saturation at high applied fields. The authors of [4] demonstrate both experimentally and through simulations that the emitter current saturation is due to a large voltage drop along the CNT emitter and/or at the CNT/substrate interface. Our experimental results show that the last hypothesis as the most convincing may be considered.

Indeed, 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 [17], 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, in accordance with an exponential nature of the Fowler-Nordheim dependence the resistance of the interelectrode gap is reduced with the increasing of the emission current, whereas the emitter resistance is constant. This situation leads to the fact that, beginning from the certain values of operating voltage 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. This in turn should lead to intensive heating of CNT emitters due to Joule heat, particularly on structural defects and in poor contact with the substrate. As a result, starting from a certain value of temperature glow of the field emission area in the visible spectral range appears. Besides the further rise of the electrode voltage does not lead to a proportional increase in the voltage across the discharge gap, what eliminates the possibility of exponential increase of the emission current in the interelectrode gap.

Thus, it can be stated that the main reason for the emission current limitation (effect of current saturation) is the high internal resistance of CNTs and CNT- substrate contact junctions. This hypothesis is confirmed by the correlation of the beginning of current curves inflection and the intensive Planck glow of the field emission area in the visible spectral range. The appearance of glow indicates CNT emitters heating to the temperatures over 1500 K. The heating in this case is due to the Joule heat generated by current passing through the emitting nanotube array. At sufficiently large emission currents ($I \geq 10^{-4}$ A) almost all supplied to the electrodes potential falls on the CNT array and its contact with the substrate, what leads to the further emitter heating and its irreversible thermal degradation and destruction.

4. Summary and conclusions

The interrelation of the field emission current saturation effect with the field emission area glow in the visible spectral range was investigated. Field emission scanning microscope for spatially resolved CVC measurements and video camera built into the vacuum chamber of the measuring unit allowed to observe the emission region in real time.

It was found that the main reason for the emission current saturation can be associated with a high internal resistance of the CNT array. This is evidenced by the overlap of the beginning of the Fowler-Nordheim curves inflection and the intense glow of the electron emission area in the visible spectral range. For sufficiently large emission currents almost all supplied to the electrode potential falls on the CNT array and its contact with the substrate, what limits the possibility of further increase of the emission current.

Thus, to avoid the effect of the field emission current limitation of the CNT FECs a search of synthesis technology of carbon nanotubes with low electric resistance, minimal structural imperfections, unified geometric parameters (height, diameter, distance) on the entire working area of the cathode is required. Solving these problems will pave the way to obtaining high emission current densities for CNT FECs, required for creation a new generation of instruments and devices of vacuum microwave nanoelectronics.

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