Some peculiarities of high emission current from CNT-polymer composite

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Abstract. We explore field emission properties of a new class of the emitters formed by coating the CNT-polymer composite film onto the flat metal substrate. At present we succeeded to obtain 125 mA for the field emitter diameter of 1 cm at the half-period sine voltage of 50 Hz.

1. Introduction

It is known that a single tip in a field (not explosive) emission allows to yield current density practically equal to electron stream towards the solid-vacuum boundary [1]. According to the measurements of electrical conductance [2], individual CNT is capable to sustain the current amounting to 2 mA. This value corresponds to current densities $10^7$-$10^8$ A/cm². Experimentally observed ultimate field emission current from individual CNT amounts to ~100 μA [3].

Taking into account the moderate emission current (~10 μA) from individual tip, the great number of potential emitters from CNT must allow to get total emission current up to 100 A from 1 cm² area. By present time there is a series of the experimental works in which the current density level close to the theoretical value is reported. For example, in [4] the current density up to 1 A/cm² for 16 emitters with area 0.5x0.5 mm² each is shown. The density of vertically standing CNT was $10^6$cm⁻². Peak values of the current of 30 mA at modulation frequency of 1.5 GHz and 29 MV/m field intensity were achieved. In this connection, the decrease in measured currents for larger emitter areas (up to 1 cm²) seems to be unexpected. The record figures reached for emission are presented in [5]. For real emitters with total area about 1 cm² these values are less than 1 mA.

2. Experimental technique

The methodology of the experiments is described in [6,7]. The experimental setup bases on turbo-molecular pumping and provides quick replacement of the samples.

We used tablet-like sample 1 cm in diameter made of different metals and graphite as a substrate for the emitter. The field emission (FE) experiments were carried out in standard diode construction with flat electrodes. The luminescent screen was positioned just behind the grid-anode. The current behind the grid was registered by substituting the luminescence display with Faraday cap.
Large dissipated energy in our power supply regime made us to apply massive anode. We used the same tablet-like sample as an anode. Paper [7] reveals that the bipolar power supply introduces new properties of emitter and may form emission structure on the opposite electrode. According to the data published earlier [8] the emission currents about 1 mA and more lead to considerable material transfer onto the neighboring electrode (most probably CNT’s or their fragments). In order to effectively remove heat the anode was placed inside the heavy stainless steel holder. Everywhere in the experiments we used vacuum inter electrode gap from 200 μm to 1 mm without special spacers. The voltage-current characteristics are convenient to observe by oscilloscope in the regime with highly repetitive low frequency pulse, e.g., provided by power supplying outlet 50 Hz. This method for field emission investigation by high voltage scanning and computer data recording was reported previously in [9].

3. Emitter preparation
In our work we study FE properties carbon nanofillers-polymer composite films deposited onto the flat metal substrate. The PS-MWNT composite was prepared by mixing rated amount of PS-xylol solution with the rated amount of MWNT-xylol suspension. We used MWNT produced by Arkema (http://www.arkema.com). To make the suspension uniform ultrasonication up to one hour was applied. PS-MWNT suspensions were coated onto the polished stainless steel tablets by means of spin-coating technique.

4. Experimental results and discussion
In order to optimize PS-MWNT composite preparation conditions we used data about emission centers distribution uniformity in small currents regime (up to several mA), that were gained from the analysis of the luminescent screen. It is also convenient to observe the beginning of FE and, accordingly, the threshold values of an electric field on luminescence screen. The view of the luminescence screen in a mode of initial currents (some mA) is shown on fig.1. However, in our experiments the threshold of FE is a voltage when a value of current exceeds 10 μA. These values of current guarantee that we observe FE from more than one nanotube.

![Figure 1. Examples of the screen luminescence: a) current <1 mA; b) >1 mA](image)

Further investigations were made with various grids and a Faraday cap. Use of a grid and Faraday cap in microampere current regime allows to exclude the influence of a capacitive component of a measured current (fig.2a). The latter becomes rather noticeable in situation with the large surface of emitter and microampere currents. Furthermore, the use of a grid and Faraday cap allows to ensure the field character of electron emission. We applied various grids enabling the significant warming up. With 50% transparent grid the currents 20 mA were output.

The study of PS-MWNT emitter was carried out in a mode of short pulses in a wide range of duration and repetition frequency (fig.2b). For this purpose the solid-state high-voltage pulse generator based of IGBT transistor was developed and made. The obtained results have shown lack of a possible temperature influence which could arise from power dissipation at the anode in a mode of sinusoidal feeding. As well we excluded the assumed heat emission component of emission current. One can see
from the figures, that the back front of current pulse has a significant reactance with drop of emission current, as was discussed previously.

Fig.3 represents the voltage current oscillogram of PS-MWNT emitters written on computer in high current mode. The distance between electrodes was 500 microns. The FN-plot has no knees of characteristic [10] which additionally indicates the absence of great heating of carbon nanotube tips.

**Figure 2.** Voltage current oscillogram of PS-MWNT emitters: a) written on Faraday cap; b) in the mode of short pulses

![Oscillogram](image)

**Figure 3.** Voltage-current characteristic of PS-MWNT emitter: a) oscillogram written to computer; b) Fowler–Nordheim dependence

![Characteristic](image)

SEM photography of initially prepared PS-MWNT sample is shown on fig.4a. The figure demonstrates that MWNT do not rise over the surface. As follows from the figure, nanotubes lay on the surface and apparently, are slightly immersed in a polystyrene. Possibly, the same pattern was observed in [11]. However, in our case we found out a significant surface modification after field emission experiment (fig.4b).

As is seen, the nanotubes protrude over the surface. The walls of the nanotubes and of their tips are fairly thin and seem to be free from the polymer material remanents. We attribute the protruding of the nanotube over the material surface upon FE experiment to the peculiarity of the composite preparation. These peculiarities may for example enable the tubes to remain mobile inside the PS matrix. The nanotube can therefore be considered as a dipole which can reorient in electric field [12].
5. Conclusions
1. We show that PS-MWNT composite coatings have several attractive features important for development of cheap field emitters with big values of emission current, big surface area and fairly stable in vacuum. PS matrix provides with the good adhesive properties to different substrates. The use of nonaligned nanotubes makes it easier and cheaper the formation of the emitter as well as provides a stable work of the emitter in technical vacuum conditions. The emitter is stable to sporadic local bursts without the decrease in its emission properties. We attribute the ability of the emitter to recover its properties to the very large number of the separate nanoparticles as well as to the possibility of their orientation in the electric current during the experiment. MS studies show high stability of the PS matrix upon the work of the emitter in high current regimes.
2. We have obtained the stable emission currents $\geq 50-100$ mA. The protruding of the tubes over the surface (SEM data) results in the simultaneously function of numerous emission centers in the single emission experiment. The use of short pulses to exclude the heating of anode as well as the coating preparation regimes' optimization may hopefully lead to higher FE current values.

6. Conclusions
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