

# Hysteresis phenomenon of the field emission from carbon nanotube/polymer nanocomposite

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**Abstract.** Using the high voltage scanning method and the technique of multichannel recording and processing of field emission (FE) characteristics in real time mode we found out some subtle effects on current voltage characteristics (IVC) of the multi-tip field emitters. We observed the direct and reverse hysteresis simultaneously in the same field emission experiment. Dependence of the form of IVC hysteresis on time of high voltage scanning was observed.

## 1. Introduction

The field emission phenomenon is an inertialess process [1]. The basis of its study is the quantum-mechanical model of the tunnel effect, proposed by R. L. Fowler and Nordheim in 1928. This model describes well the field emission from the metal single-tip and multi-tip systems. To obtain reliable current-voltage characteristics of such systems was enough to measure the current in the range of several orders of magnitude. However in the past two decades with the advent of the huge variety of nanostructured materials and its nanocomposites, the results and interpretation of emission properties investigation became more complicated. This has led to a change in approach to the study of the emission properties of the objects, namely, repetition of the voltage-current characteristics of the passages with a cyclic increase and decrease in applied voltage. As a result, it began to appear a significant amount of work, indicating the presence of hysteresis in the obtained current-voltage characteristics.

For a single multi-walled carbon nanotube in the paper [2] was obtained IVC hysteresis, when at the falling branch of the voltage currents exceeding the current rising branches were observed.

There is an article about IVC hysteresis of emitter based on graphene sheets [3]. The effect of differences between branches of applied voltage is most noticeable on the FN plots. The study shows that a more rapid impact of high voltage leads to a broadening of the hysteresis loop. Hysteresis effects are explained by the balance between Joule heating and sorption processes.

In paper [4] the hysteresis of carbon nanotube fibers was investigated. The various field emission modes are identified in the forward and reverse sweeps and related to changes in the fiber morphology.

Oriented aluminum nitrides on a tungsten tip in [5] demonstrate hysteresis when the current on the falling branch less than on rising branch. The explanation is the charging of the insulating AlN layer films, when the electrons emitted into the vacuum are not compensated by electrons from source.

Discussion of the influence of adsorbed molecules on the appearance of hysteresis in an array of non-oriented CNT grown on a nickel substrate, is given in [6]. In this paper three types of adsorption



were considered: internal adsorption, stimulated by the field and stimulated by the current. The dependence of the hysteresis of the vacuum level and the speed of the voltage was found. It is shown that the hysteresis decreases with increasing vacuum level.

There was a decrease in the emission current at the falling branch of the applied voltage for the array of carbon nanotubes coated with titanium [7] and tantalum. [8] It was shown that with increasing duration of the scan voltage, the hysteresis loop is expanded to lower currents. The special 'eight' shape of IVC was registered in [9] for CNTs.

The examples of works show that hysteresis appears in two basic ways: when the current of falling branch less than rising branch (so-called direct hysteresis, the most frequently observed in carbon nanotubes) and reverse hysteresis when the current with decreasing voltage become higher than the rising branch.

## 2. Experimental details

We investigated thin film field emitter consisted of polymer / carbon nanotube composite. The technique for characterizing multi-tip field emitters was described in detail in our paper [10]. It includes the original program of multichannel recording and processing of data, written in LabView 2013. The power source is controlled by a computer FID Technology power supply. The rate of voltage change is set by the DAC board NI DAQ PCIe-6351.

For sample preparing we used two different types of nanotubes: MWCNT by Samsung (according to SEM length of tubes is  $\sim 10 \mu\text{m}$  and diameter is  $\sim 19 \text{ nm}$ ) and SWCNT (length of tubes exceeds  $10 \mu\text{m}$  and diameter is  $\sim 2 \text{ nm}$ ). Firstly CNT powder was treated in an ultrasonic bath in o-xylene for 8 hours. Then this suspension was mixed with polystyrene solution and again was treated in the ultrasonic bath for 8 hours. Finally thin film of field emitter was deposited onto metallic substrate by spin coating technique.

Figure 1 and figure 2 shows SEM images of the created emitter surfaces: polystyrene with multi-walled nanotubes – "PS-MWCNT" and with single-walled nanotubes – "PS-SWCNT".

## 3. Results and discussion

We have previously shown that the shape of the scanning pulse voltage applied to the sample does not influence on the current-voltage dependence significantly [11]. In this study, we used only pulses with a triangular profile.

Research can be divided into two subgroups:

- 1) study the effect of the scanning voltage pulse duration on the IVC of different samples;
- 2) study the effect of the voltage pulse amplitude in the direction of the IVC hysteresis.

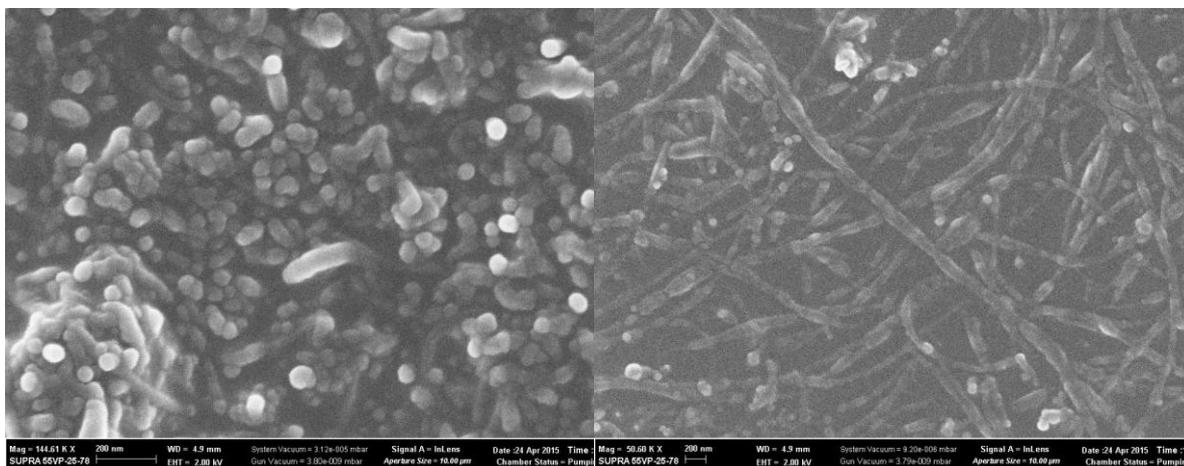


Figure 1. SEM image of PS-MWCNT sample

Figure 2. SEM image of PS-SWCNT sample

3.1. Effect of change in the scanning pulse voltage duration on the IVC

Figure 3 shows the shape of the scanning pulse voltage and the IVC of the PS-MWCNT sample. There is a hysteresis typical for many similar multipoint field cathodes hysteresis where rising branch passes over a falling branch (the so-called "direct" hysteresis).

Note that the repetition of this experiment leads to the almost complete repetition of the IVC in figure 3 (except for noise roughness).

Figure 4 shows the same IVC in the Fowler-Nordheim coordinates. There is the same hysteresis, but curve has also a characteristic crooked tail at low currents, which cannot be described by the known Fowler-Nordheim law for cold field emission.

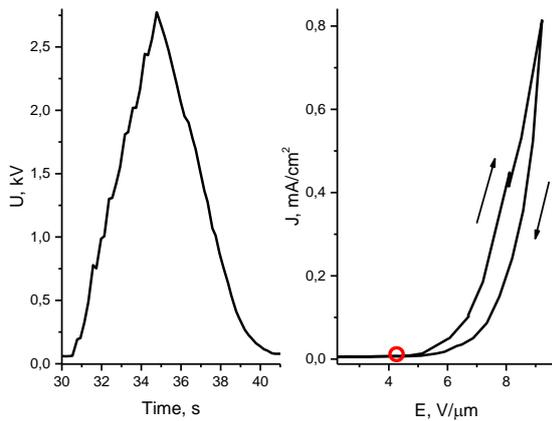


Figure 3. Example of a high voltage pulse and corresponding IVC for PS-MWCNT sample

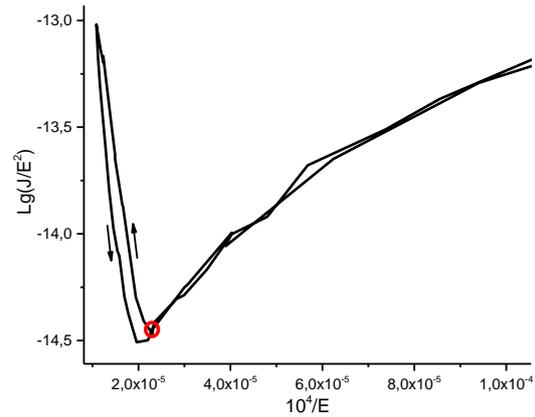


Figure 4. The IVC for PS-MWCNT sample in FN-coordinates

Figure 5 and figure 6 show the result of an experiment on the effect of the scanning pulse duration on the IVC of the sample PS-MWCNT. The graphs show that with increasing pulse duration the intersection point of the falling branch and rising branch appears in the "direct" hysteresis of IVC and gradually move to the high voltages.

Similar experiments with the PS-SWCNT sample showed that intersection point of the IVC branches for composite with single-wall carbon nanotubes appears at shorter pulses than for composite with multi-wall nanotubes (see figures 7, 8).

Note that the threshold voltage for PS-SWCNT is lower than for PS-MWCNT, which can be related with a smaller radius of the electron-emitting nanotips.

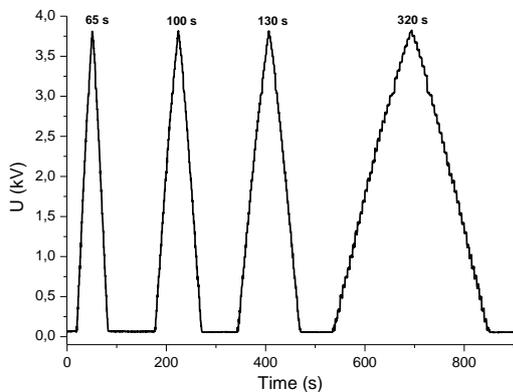


Figure 5. Sequence of slow pulses of voltage applied to PS-MWCNT sample with different pulse duration (see digits above)

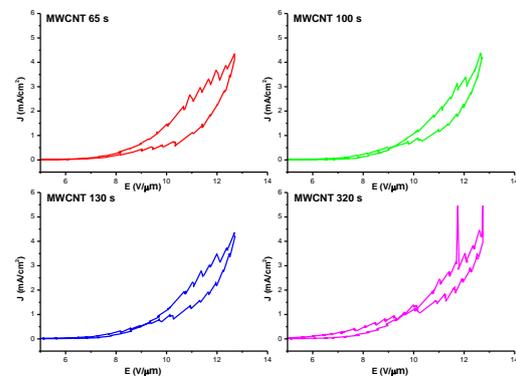


Figure 6. The "eight" shape hysteresis formation in IVC for PS-MWCNT sample at different pulse duration

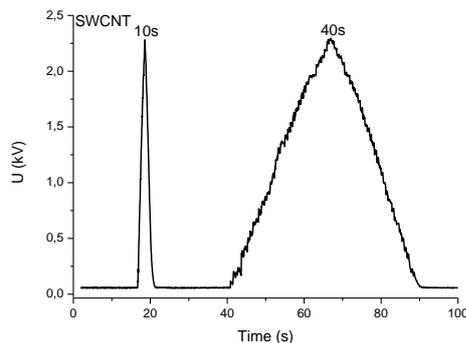


Figure 7. Sequence of slow pulses of voltage applied to PS-SWCNT sample with different pulse duration (see digits above)

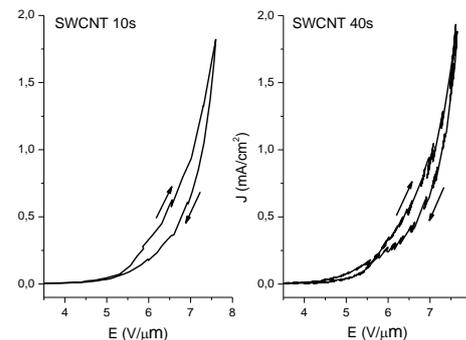


Figure 8. The "eight" shape hysteresis formation in IVC for PS-SWCNT sample at different pulse duration

### 3.2. Effect of change in the scanning pulse voltage amplitude on the IVC

In a second series of experiments we tried to find out the effect of change in the amplitude of the scanning pulse voltages, as well as their consecution on the shape of the IVC for PS-MWCNT sample.

Figure 9 shows three following each other voltage pulses with different amplitudes (the amplitude of each pulse is greater than the amplitude of the previous). Figure 10 shows the corresponding IVCs.

The graphs show that with increasing amplitude the IVC naturally increases and the difference between rising and falling branches of "direct" hysteresis increases too. Quite a different picture is observed with a gradual decrease in the amplitude of the pulse.

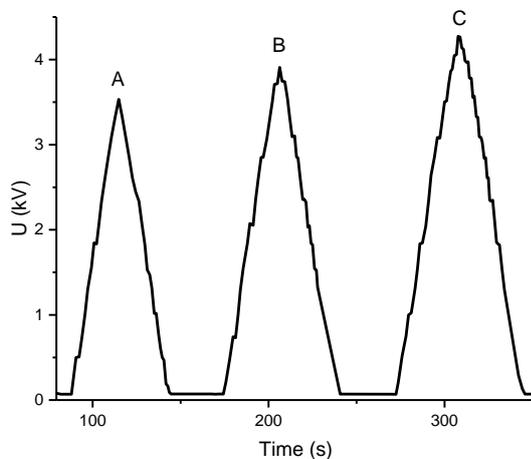


Figure 9. Sequence of slow pulses of voltage with different amplitudes applied to PS-MWCNT sample.

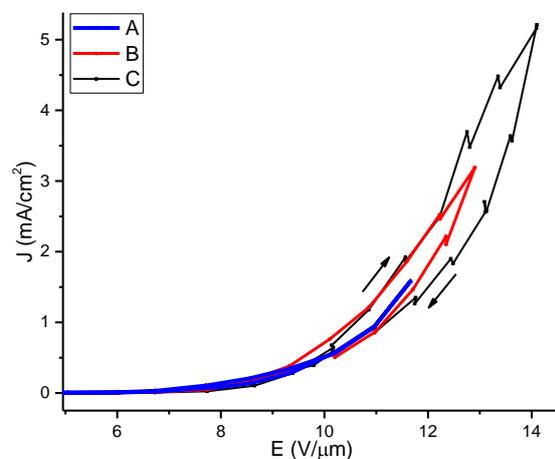


Figure 10. Change of IVC hysteresis with increasing pulse amplitude for PS-MWCNT sample.

Figure 11 shows the two following each other voltage pulses of different amplitudes (the second lower than the first) applied to the same PS-MWCNT sample. Figure 12 shows the corresponding IVCs. This experiment was repeated several times and each time with decreasing the pulse amplitude "direct" IVC hysteresis changed its direction turning to so-called "reverse" hysteresis, where a rising branch is held under the falling branch.

At the same time consistent decrease in the pulse amplitude retains the direction of the hysteresis - every pulse there is a "reverse" hysteresis (see figures 13, 14). Also, it was noted that the time delay between the pulses did not affect on the direction of IVC hysteresis.

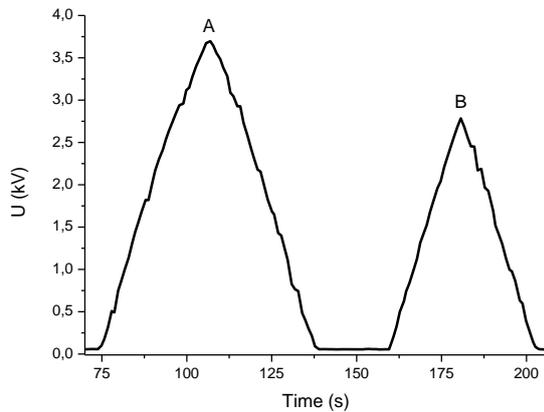


Figure 11. Two pulses of high voltage with different amplitude applied to PS-MCNT.

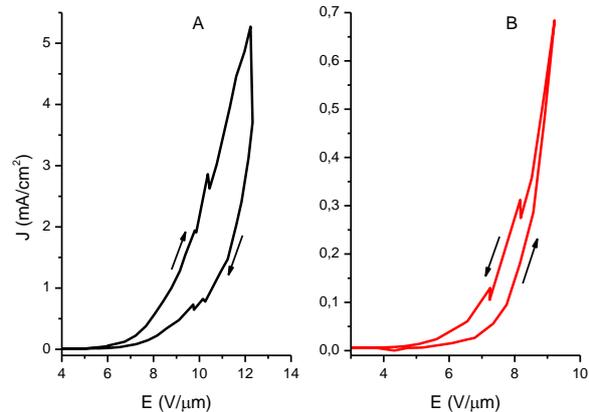


Figure 12. Change of IVC hysteresis direction after reducing of voltage pulse amplitude for PS-MCNT.

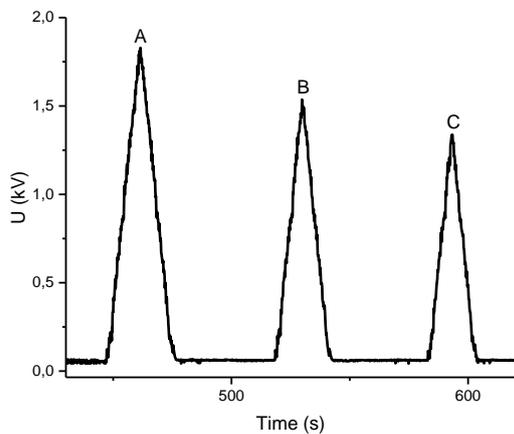


Figure 13. Three pulses of high voltage with different amplitudes applied to PS-SWCNT sample.

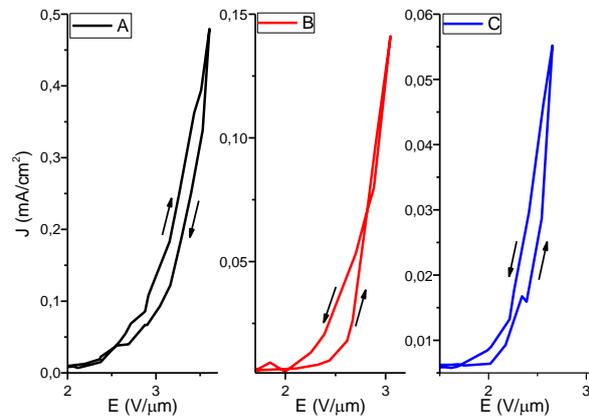


Figure 14. IVC hysteresis for three high voltage pulses with different amplitudes applied to PS-SWCNT sample.

Maintaining the pulse amplitude at a constant level leads to inevitable disappearance "reverse" hysteresis rise "direct." An example of this effect is shown in figure 15 and figure 16.

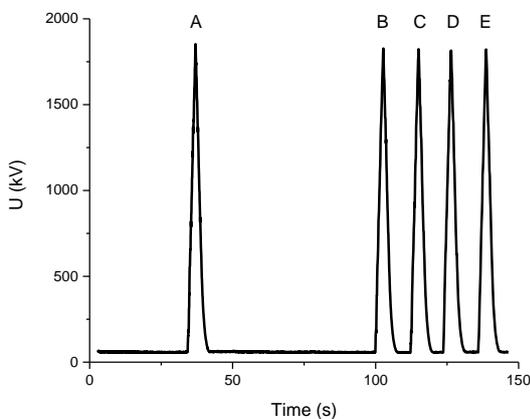


Figure 15. Two impulses of high applied voltage with different amplitude

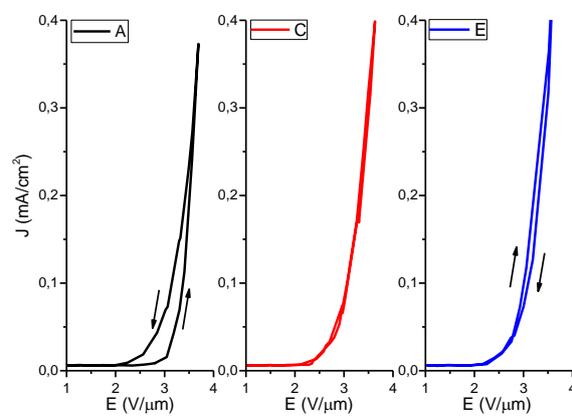


Figure 16. Change of IVC hysteresis direction after higher voltage applying PS-SWCNT

#### 4. Conclusion

We managed to register the following effects connected with IVC behavior of nanocomposite field emitters:

- 1) In a mode of slow voltage change (an order of ten seconds on an impulse) the appreciable hysteresis is observed in the IVC.
- 2) The increasing in impulses duration leads to steepness change of a IVC falling branch and to emergence of an intersection point of falling and raising branches.
- 3) Using single-walled nanotubes in nanocomposite leads to earlier emergence of intersection point (at smaller duration an impulse).
- 4) Gradual growth of impulses amplitude keeps a direction of a hysteresis.
- 5) Amplitude reduction leads to emergence of a reverse hysteresis.
- 6) At maintenance of impulses amplitude the return hysteresis gradually disappears, turning to a straight line.
- 7) Delay time between impulses does not influence on the hysteresis direction, the important was only the previous voltage pulse amplitude.

Many works assume presence in nanocomposite materials a percolation effect associated with local charging of emission nanotips, separated from the cathode with the dielectric layer of polymer that can influence on emitting ability of a sample surface and to cause emergence of the IVC hysteresis.

Emergence of a point of intersection of growing and falling branches in a hysteresis can be associated with participation in emission process one more effect – thermionic emission.

Point 2 in the list resulted above confirms a hypothesis of presence of the thermionic emission contribution as at increase in duration of impulses nanotubes have time to heat up and the return branch IVC starts to cross a straight line.

Point 3 also confirms this hypothesis therefore as radius reduction nanotubes should lead to their faster warming up and consequently the thermionic emission contribution to a falling branch IVC becomes more powerful.

So, we assume that not only percolation effect can lead to IVC hysteresis emergence, but also thermionic emission is responsible for its appearance.

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