The emission characteristics of graphene in different modes of high-voltage power supply

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Abstract. We found out the general laws of the current-voltage characteristics hysteresis behavior for emitters of different nanomaterials – graphene, nanotube. Comparison of two power supply modes showed that the IVCs change with growth and decrease of the scanning voltage amplitude in "fast" mode which correlates with current-voltage characteristic hysteresis in "slow" mode. Common patterns forms of current-voltage characteristics in different power supply modes were identified.

1. Introduction

At the recent years due to the progress in the methods of acquisition and processing experimental data the features of the current-voltage characteristics (IVC) of field emitters has been more frequently observed. One of them is so-called hysteresis effect of IVC, which still remains poorly studied. The problems seem to be associated with increasing divergence between developed theory of the single-tip emitter and real multi-tip large area field emitters (LAFE). Such emitters have a potentially huge market of practical applications in the vacuum nanoelectronics.

Before we consider the works on experimental research of the LAFE emitters, it is necessary to introduce some concepts. The emission characteristics can be measured either at increasing voltage (using definition of the threshold field) - a growing branch of the IVC, as well as at a decrease (from the maximum value of the applied voltage to the minimum) – descending branch of the IVC. Let’s call direct hysteresis situation when the emission current is lower on the descending branch of voltage in comparison with the growing one, and let’s call reverse hysteresis – situation when descending branch of voltage pulse gives a greater emission current rather than ascending one.

Apparently first who observed the effect of unsymmetrical IVC behavior were Millikan and Eyring in the field emission experiment with the stretched tungsten wire as the cathode and the cylindrical anode [1]. The main source of the features in the IVC is rightly considered the sorption of metal atoms and different molecules. Investigation of the effect of adsorbed particles on the magnitude of the emission current in the single-tip emitters were actively conducted from the middle of the last century. In Gomer's monograph [2] a simple formula connecting the change in the work function and the
number of adatoms was proposed. In 1967, Duke and Alferieff shown that resonant tunneling of electrons in a vacuum can occur through energy level of adsorbed particle [3].

The most important achievement of recent years is the question statement about the nature of the adatoms (atoms and molecules which are falling on the surface of the emitter) and the nature of their impact on the emitter work function [4]. For example, Li and Wang in [5] predicted that adsorbed CO and CH$_4$ increase the work function. Sheng [6] also showed a decrease in current at adsorption CO and CO$_2$ molecules.

Hysteresis effects of the IVCs (both direct and reverse) on carbon nanotubes of various types were observed in several papers [7-13]. Among the possible causes of the hysteresis most frequently found next ones: the influence of adsorption-desorption processes, Joule heating, the processes of adatom polarization, reversible morphological changes in the emitter surface. In [14-15] authors tried to register type of gases desorbed from the nanotubes surface in the field experiment using a mass spectrometer technique. Desorption of H$_2$, CO and CO$_2$ molecules were specified.

The effect of IVC asymmetric behavior was also observed in other LAFEs: porous diamond [16], amorphous Alq3 [17], oriented-AlN thin film [18] and different graphene materials. There are two common experimental approaches to study FE from graphene. The first one consists of local IVC measurements of graphene by single-tip anode in scanning or transmission electron microscopes [19,20]. The second approach utilizes a luminescent screen as anode and provide information about integral IVCs [21,22].

A special place in the studies took the works of Li, Chen, Yan et. al. [23-25]. The authors provided repeatable research of the new graphene materials. They observed direct hysteresis in IVCs of graphene emitters and explained this effect by adsorption-desorption processes. Targeted study of the influence of the inlet gases (oxygen, nitrogen and CO$_2$) on the field emission of graphene emitter has been provided in [25]. The authors argue that the field emission deteriorates after the adsorption of O$_2$ and CO$_2$. In [26,27] on the contrary the reverse hysteresis was observed. In [27] a lateral placement of the graphene film was used and the emission of the side faces was studied (emitter blade length was 1 cm). The hysteresis in this case was explained just by the exfoliation of the graphene film edge from the substrate.

2. Experimt
The study was conducted at a residual pressure in the experimental volume $\sim 10^{-7}$ torr. The range of the voltage applied to the sample was 0 - 6 kV. The electrode spacing (cathode-anode distance) was 300 µm. As a counter electrode we used tantalum anode. The cathode was a metal tablet with diameter 10 mm coated with nanocomposite film. As nanocomposite we used graphene sheets (G$_{111}$, NanoTechCentr TSTU, Tambov, Russia) and polystyrene as a matrix. Prepared graphene-polystyrene suspension was subjected to ultrasonic treatment for 8 hours. Then suspension was deposited onto the substrate by spin coating technique. The technique for characterizing multi-tip field emitters was described in detail in our work [28].

In article [29] we have found out that the prehistory and amplitude of applied voltage pulses define the form and the direction of a hysteresis (direct or reverse). The assumption that the direct hysteresis appears at increasing of amplitude and the reverse - at decreasing of amplitude in comparison with the previous impulse was made.

In this article both direct and reverse hysteresis’s of graphene samples have also been received.

3. Results and discussion
3.1. “Slow” mode power supply
In “slow” mode DC voltage levels were applied to the sample. Using power source (FID Technology power supply) controlled by a computer and DAC board NI DAQ PCIe-6351 we able to change voltage level and pulse duration. Figure 1 shows two voltage pulses applied to the sample consequently. One can see from figure 2 that corresponding emission current have a good correlation with pressure changes.
Figure 1. Voltage impulses applied to the sample in “slow” mode

Figure 2. Corresponding current and pressure (on inset) for pulses on figure 1

Figure 3. Corresponding IVC for the 1st pulse on figure 1

Figure 4. Corresponding IVC for the 2nd pulse on figure 1

Change of pressure in the measuring chamber along with emission current, demonstrates emergence of volatiles products in experimental volume. The source of the pressure increase could be desorption of adatoms from the emitting centers (graphene plates) or from an anode surface. Intensity of streams and speed of a response depend on the obtained emission current value indicate that electron-stimulated desorption takes place to be.

So, using this sequence of pulses we have obtained transition from direct to reverse hysteresis. Also, we have found such conditions which allow us to get transition from reverse hysteresis to direct hysteresis. From figure 5 it can be seen that two pulses with equal amplitudes can provide this transition. Figure 6 demonstrates the same correlation between emission current and pressure in the experimental volume.
Figure 5. Voltage pulses applied to the sample in “slow” mode

Figure 6. Corresponding current and pressure (on inset) for pulses on figure 5

Probably volatile products dramatically affect on the field emission process. Corresponding IVCs for these pulses are presented on figures 7, 8.

Figure 7. IVC for the 1st pulse on figure 5

Figure 8. IVC corresponding for the 2nd pulse on figure 5

3.2. “Fast” mode power supply

In fast mode the half-sine pulses with 50 Hz rate and 10 ms duration were applied to sample. The pulse amplitude $U_{\text{max}}$ was changed manually. The registration of the corresponding emission current pulses gives about 50 IVCs for 1 second.

The gradually increasing and decreasing of the voltage amplitude leads to hysteresis in the changing of current pulse amplitude $I_{\text{max}}$ (see figures 9, 11).

Figure 9. Voltage and emission current time dependences in the “fast” mode

Figure 10. IVCs at different moments for gradually rising and falling of scanning voltage amplitude
The transition from direct hysteresis to reverse hysteresis is observed at the analogue sequences of voltage pulses as for “slow” mode power supply (see figures 10 and 12).

3.3. Comparison of two power supply modes

As it can be seen from figure 13 the hysteresis of IVCs obtained in “fast” mode power supply almost have no differences from IVCs registered in “slow” power supply mode. Besides, there is match of hysteresis patterns in both modes of power supply.

4. Conclusions

It was found that the effect of a IVC hysteresis can be observed on graphene-polystyrene nanocomposite emitter. We experimentally defined the conditions of emergence of both types of the hysteresis (as direct, and the reverse). Connection of different types of a hysteresis in fast and slow power supply modes has been shown, thereby we have proved reliability of these methods of the IVC studying, and also a community of the nature of this phenomenon irrespective of a power supply mode. Taking into account work [29] we showed that behavior of the hysteresis effect is uniform for emitters of various types, for example, both for nanocomposite with use of nanotubes, and for those containing graphene as a fillers.

According to registration of vacuum and partial pressures, it is possible to take for granted the dependence of vacuum level, namely the partial pressures of vacuum level (CO$_2$) from the magnitude of emission current and not vice versa. We claim that $P(CO_2) = f(I)$ the defining nature of this dependence is electron-stimulated desorption from an anode surface. In this regard it is possible to
claim that the effect of a hysteresis practically doesn't depend on vacuum level, and is exclusive from a condition of surface electrodes purity.

From this follows that the speed of emission area change will be defined by streams of particles as a result of ESD, but not time of sedimentation of residual atmosphere gases (depends on local change of vacuum).

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