The technique of field emission parameters research for nanostructured materials improvement

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Abstract. A new technique was developed to record and in situ process the data on the evolution of multiwall carbon nanotubes polymer (MWCNT-polymer) nanocomposite field emitters. It includes multichannel acquisition system of current voltage characteristic (IVC), vacuum level, temperature and mass-spectrum data with computer on-line processing of these data based on the LabVIEW program. We obtained the time dependence of the field enhancement factor, the number of emission sites and kinetics of main volatile products during field emission process.

1. Introduction

Carbon nanotube (CNT) polymeric nanocomposites as field emitters are now being evaluated for a wide range of vacuum electronic applications. Due to excellent field emission (FE) properties of CNTs, they can be used as unheated cathodes for X-ray sources, field emission displays, luminescent mercury-free tubes and vacuum triodes [1-5]. In spite of significant success in practical implementation of CNT for FE, many important problems have not been solved yet. Now it is very difficult to make a reliable conclusion concerning the physical processes occurring on the surface of nanosized emission sites by measuring macroscopical current and voltage values. Besides, additional difficulties arise in the study of field emission dynamics, when a change of the studied object or its environment may occur.

It is known that the investigation of carbon emitter stability is a multiple parameter problem, with a change of vacuum conditions and emitter surface temperature to be taken into account. Therefore the question of particular interest is registration of the phenomena accompanying functioning of flat multi-tip cold emitters, such as detecting an emitter radiation, visualization of emission sites distribution, field electronic microscopy and registration of volatile products by mass spectrometer.

Today, recording and processing of current-voltage characteristics (IVC) constitute a basic tool in the study of the materials promising as efficient field emitters. The computerized data acquisition systems used for these purposes are very effective. This allows better understanding of IVC dynamics and their correlation with the other emission phenomena.

The direct (on-line) processing of emission characteristics throughout the experiment was rarely used [6, 7]. For example, the work [8] describes the application custom LabVIEW program to the study of carbon nanosheets field emitters. The authors used the mass spectrometer for measuring partial pressures of reaction products. In addition, the similar method was used in [9]. The authors designed vacuum system in a cathode-anode configuration in line-of-sight to a residual gas analyzer. The data were recorded under LabView control.
We succeeded in developing the technique of multichannel recording and on-line processing of data on the field emitter evolution. On-line processing of signals has been performed on the basis of our program written by LabVIEW 2012.

2. Experimental details

As an object of research we used the nanocomposite polymer - multiwall carbon nanotube emitter (MWCNT-polymer) that has already shown remarkable properties: high values of emission currents, stability to the vacuum condition and sufficient stability of emission parameters [10]. This nanocomposite emitter easily enough forms the emitting surface of a large area with a good adhesion to the conducting substrate.

To make the samples we used a MWCNT suspension. As nanotubes we use certificated Graphistrength® MWCNT by Arkema firm (according to SEM, length of tubes is up to five microns, diameter is up to 15 nm) and as a polymer - polystyrene (PS), -polymethylmethacrylate (PMMA) and nitrocellulose (NC).

Suspension of MWCNT in a polymeric matrix was prepared by mixing of nanotubes suspension and 1 % polymer solution in the same solvent. Weight concentration of tubes in a polymeric matrix was taken equal to 10 %. Mixing in an ultrasonic bath for 8 hours was applied to prepare suspensions. Drawing of an emission surface on the flat substrates of stainless steel was made by spin coating technique. The field emission experiments were carried out in standard construction with flat metal electrodes.

To obtain IVC of the sample the high-voltage power unit with frequency 50 Hz was used. Electronic rectifier made positive impulses with duration 10 ms and consequently one such half-sinusoidal impulse gave one IVC. Other researchers in work [11] for the hardware analysis of IVC-FN evolution used a close idea.

Measurements were carried out at a cathode-anode gap \( d = 300 \mu\text{m} \) and various amplitudes of sinusoidal voltage impulse (thereby the range of amplitudes of corresponding current impulses was from 1 \( \mu\text{A} \) to 10 mA). Management of a high level voltage and change of interelectrode gap was carried out by means of the laboratory autotransformer and the micrometric screw. The system was evacuated to a base pressure of \( 5 \times 10^{-7} \) Torr.

To obtain mass spectrum signal we used reflectron type time-of-flight mass spectrometer (TOF-MS). The neutral molecules formed upon decomposition of the polymer (for PMMA and PS these are mainly the respective monomers) are ionized by the electron impact. For electrons of 70 eV the mass-spectra are tabulated. The TOF-MS is equipped with oil free pumping system and microchannel plate detector.

The measurement technique includes multichannel gathering system that records and sends to the personal computer values of emission current, anode-cathode voltage, cathode temperature, pressure and full mass spectrum signal (Figure 1). For this registration a multichannel plates DAQ by National Instruments NI PCIe-6351 are used.

The cathode temperature at high voltage is registered by multimeter UNI-T UT60G with optocoupling. For the purpose of computer plug-in-card protection against the vacuum breakdowns, measured and operating signals were directed through the multichannel block of protection and amplification. The synchronization was made by digital trigger formation scheme depending on the outlet supply phase. Thereby huge stream of IVC realizations that were in each period of scanning by the high voltage impulses was reached.

The computer analysis and recording of IVC evolution in time was carried out by own program written by LabView 2012 (figure 2). Program includes blocks that calculate and allow to observe a form of voltage and current impulses - \( U(t) \) and \( I(t) \) in real time mode, current-voltage dependence - \( I(U) \), dependence of current density from electric field intensity - \( J(E) \), IVC curve in Fowler–Nordheim coordinates - \( Y(X) \) and its diagram in the slope-intercept coordinates - \( S(K) \) (Seppen-Katamuki analysis [11,12]). Also it allows to control both the composition and kinetics of main volatile products.
Additionally, data for representation in a convenient for the analysis form were processed: time dependence of the emitter power, time dependence of an emission interval active resistance and current loading on one MWCNT. The visualization of emission sites effective height and their number also was carried out.

The calculations were made by formulas from the known monograph with the same constants and values dimension [13]. The obtained data were deducted on plots of time dependences: $\beta(t)$, $N(t)$ and $h(t)$. For emitting site number evaluation we used the emitting area of the individual MWCNT which was offered in work [14]: $S_{\text{CNT}} = 1.8 \text{ nm}^2$ for individual MWCNT with diameter 15 nm. In our work we apply MWCNT of the same diameter. As shows the further reasoning this estimation gives quite adequate values of number of the emitting sites.

In our technique, we tried to work at high levels of current when field emission current much more than capacitive component. At small emission currents (several $\mu$A) a record and subtraction of parasitic capacitor "support" from the signal was used. Besides for increase in accuracy of measurement our program made accumulation and averaging profiles of current and voltage impulses in set time interval (about 100 impulses were averaged for 5 seconds).

The described apparatus has allowed us to obtain a number of promising results for field emitters. Some of them are shown below.

3. Results and discussion

Figure 3 demonstrates the characteristics recorded for MWCNT-NC emitter: time realizations of applied voltage, emission current and the main volatile products intensity registered by TOF-MS. In our experiments thermal instability of the sample was observed in mode with large emission currents (more than 10 mA). Intensity of main volatile product in the mass spectrum increases gradually: see kinetic of the peak $h_{30}$ (fragment of nitrocellulose monomer) in the mass spectrum in figure 3. This increase points out that the gradual destruction of the polymer matrix occurs.
Figure 3. The characteristics record of MWCNT-NC emitter: integral (U, I) time realizations and
the main volatile products registration

Figure 4 shows the SEM images of a MWCNT-NC emitter surface before and after FE experiment.
One can see that the thickness of the polymer surrounding nanotubes has reduced significantly from
~74 to ~58 nm. It indicates that polymer destruction occurs right around the nanotubes. We suggest
that this process is caused by the Joule heating of emitting sites.

Figure 4. The SEM images of a MWCNT-NC emitter surface before (left half) and after (right half)
FE operation

Aside from slow partial pressure change during the emission process, we also observed short-term
ejections and accompanying sharp changes in the emission current and vacuum (figure 3). It is well
known that this effect is connected with vacuum discharge and emission site degradation.

With the built-in video camera we observed the bright flashes that appear on the surface of the
adjacent electrode. This glow can appear if something conductive protrusions are formed onto the
surface of anode and electrons emitting from cathode impact them. We suggest that those protrusions
are formed due to transfer of nanotubes from composite-covered electrode to adjacent electrode.
Transfer of nanotubes is caused by "field decomposition" - influence of high electric fields on the
emission sites.

The formation of carbon nanostructures (whiskers) on the anode as a result of mass transfer is of
particular interest because it greatly restricts the emitter work. The application of high voltages leads
to overheating and burning whiskers, accompanied by a vacuum discharge and breakdown of the
system. In addition, the whiskers do not allow the use of this cathode system as the diode because they
themselves are emission centers in reverse polarity mode.

For registration of the whiskers formation, we installed a clear adjacent electrode and applied a
voltage of reverse polarity to the system. Thus we can register "reverse" emission current produced by
whiskers on the anode.

Figure 5 demonstrates the result of our experiment. With stepwise voltage increases the current
stepwise increases too with short sequence of discharges. And the time realization of the pressure in
the vacuum chamber has accompanying sharp peaks.

The SEM image of the adjacent electrode received after the experiment (figure 6) shows that not
only nanotubes, but clusters of nanotubes and polymer material were transferred to the anode.

4. Conclusion
We have developed a method of multichannel acquisition and online computer processing of data on
the evolution of working characteristics of flat multipoint field electron emitters. The jointed use of
MS and FE techniques is suggested. In situ studies open new possibilities of FE research:

- the opportunity of observation the “activation” of the samples upon the initial stages of the FE;
- the opportunity of the research of the material transfer to the counter electrode;
- the long term study of the emitter working regime;
- the thermal decomposition of the electrode materials.

By using TOF-MS we detected the presence of monomers in the volatile products emitted from the
sample surface of nanocomposite emitters at the large emission current. Moreover SEM analysis was
shown that the gradual polymer destruction occurred right around the nanotubes.

We registered the transfer of the large clusters from nanocomposite material of cathode to the
adjacent electrode. For registration of whiskers formation, we used the reverse polarity in the system.
Thereby we observed electrical evolution of the whiskers on the anode during their growth.
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