AUTOEMITTERS AND SENSORS BASED ON CNT CHARACTERISTICS EXPERIMENTAL RESEARCHES.

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The work, introduced in this report, was connected with creating of nanotubes growth technology development with the purpose of effective autoemitters, based on CNT.

While designing the nanotubes growth modes we were guided by growth mechanisms of CNT, which are known on the present moment. The carbon nanotubes growth necessary factor is the presence on the substrate of catalyst stratum, which thickness determines the nanotubes diameter, which grows on it. It is related with that, during metal film melting its thickness will define drops gage, which the film will be transformed in. Also, the researches carried out in the NIIFP (it's the institute where I pass my probation period) allows to find out correlation between drops scale and heating temperature. Experimentally was shown, that carbon nanotubes diameter directly depends on the catalytic drops size. The metal film transformation into the drops occurs while heating the sample up to the temperatures of 500 degrees centigrade or higher. It should be mentioned, that melting temperature also depends upon the metal film thickness.

After the catalyst film transformed into the great number of liquid melt drops, a working carbon-bearing gas fed inside the chamber and than dissociated into separate hydrocarbon radicals in UHF plasma. Those C-H groups and also single carbon atoms get to the catalyst particle surface, where dissociation of hydrocarbon radicals occurs and then carbon atoms diffuse into the metal. Step-by-step, carbon reaches the saturation threshold regarding its content in catalyst and then precipitates as a phase, what initiate nanotube growth. The value of this critical concentration can be decreased by the lowering of melt temperature that has already absorbed carbon atoms.

Due to this mechanism, two nanotubes grow modes was offered:

1) "Low temperature" mode, in which carbon-bearing gas is injecting into the chamber previously heated up to the 530 degrees centigrade. The additional heating is not carrying out.

The feature of this mode is that the carbon-bearing gas stream while supplying C-H radicals to the catalyst surface, cooling its surface at about 50 degrees centigrade at the same time. With this, critical concentration value reduction occurs.

2) "High temperature" mode, which concludes in that the work chamber heating up to the 580 degrees centigrade and higher. And additional heating is carrying out after the working gas has been injecting, to compensate its cooling effect.

A growing plant constitutes a chamber with forevacuum eviction ability, working gas injection system and presence of UHF plasma. Industrial butane was using as the working gas.

In this plant vertically oriented nanotubes growth on silicon, sapphire or polikor substrates was producing, with Titanium and Vanadium buffer layers combination. Nickel was using as a catalyst.

The measurements were held on the test bench with oil less vacuum eviction. It is able to evict working chamber volume to pressures at about ten in the minus six power of mercury millimeters in this system. There was a measurement mini-table that was put in to the chamber, on which power bussing of pattern had been realized and the collection area of emit electrons had been picked out.

The next autoemission parameters were measured:

- threshold voltage E_{thv} (given in the tables in corrected to the micrometers value)
- threshold current I_{thc} (the starting autoemission current)
- maximum emission current I_{max}
- medium emission current I_{med} (current that suites to the stable emission current)

Also, the patterns from which satisfactory current and voltage values had obtained, were analyzing upon the emission current degradation presence.

Further the tables are representing on the slides, that are contains growth parameters of the patterns and their measurement results. The best values of the autoemission parameters are shown in the Table 1. In the threshold voltage it is 1,5 – 2 volts per micrometer and the maximum currents reached is about fifty microamperes that has been gained from the area of one square micrometer. The next table consists of the data from patterns, which revealed the worst emission parameters. And, finally, medium voltage and current values are shown in the Table 3.

The priority for our aim, exactly for creating of effective autoemitters, – to obtain low threshold voltages of autoemission. Tables cited above show, that in general the least threshold voltages had been obtained from the patterns, which were grown by the “Low temperature” mode. And for the “High temperature” mode the higher threshold voltages are typical, in spite of one exception that is in the Table 1. The sample, which showed the least threshold value – 1,5 volts per micrometer.

One more important moment for biosensor working is a low noise level during autoemission. In the previous report there was theoretical estimate of shot, thermal and temperature noises. And the conclusion had been made, that the value of these noises are so small that they won’t influence on the biosensor characteristics. But, the experiments showed that for autoemitters with vertically oriented carbon nanotubes high level noise presents. This is relating with emission current fluctuation. The diagram that is illustrating this noise represents on the slide. The nature of this noise is most probably next. As you maybe know, not all nanotubes that have grown on the substrate will emit. For example, from the area of one square millimeter, where can be located thousands of CNT, only few (about several tens) will make contribute in to emission current. Because of some of nanotubes (their tip) are closer to anode. Also nanotubes may differ by diameter, and the thinnest nanotubes will easily emit electrons than that with bigger diameter. In the NIIFP some experiments were held with the purpose to investigate the maximum emission current that can be obtained from single nanotube. The result: 0,7 - 1,3 µA from one nanotube. So, if we have 50 emitting nanotubes we will have emission current in the range of 50 µA. BUT! The number of emitting nanotubes permanently changes, thus causing emission current noise.

This problem had been offered to solve by changing autoemitter construction. It is represents on the slide. The constructional feature is that the catalyst layer had been covered by noncatalytic material from all sides and then had been etching from the butt-end. As a result, carbon nanotubes grew only on the open side of the catalyst, thus forming some kind of the “blade”. With such configuration, the noise that relates to periodic changing of emitting nanotubes number, significally reducing. Moreover, this construction allows manipulating the nanotubes diameter, by changing catalyst layer thickness, what is also important.

There is one more problem that presents both in “vertical” and “lateral” types of autoemitters. This is the emission current degradation. The table with degradation data represents on the next slide. Here, the voltage, at which degradation was observed, pointed in the second column. In the next columns pointed out the observing time of degradation and the emission currents at the beginning and at the end of this time interval.

One of the cases when the emission current increases, what was observed for pattern named K19, can be explained by destruction of number of nanotubes during the observation time. This has leads to thinning of substrate that densely overgrown with nanotubes (the nanotubes growth time on this pattern was about forty minutes). The result of this was “sharpening” of electric field.

The degradation hypothesis can be approved by simple visual inspection of the pattern surface. You can see this bald circle on the photo. The black matter here is a nickel on which carbon nanotubes had been grown. This circle has appeared after the emission current measurements from the sample. It will be logically to ask whether such circles would appear after all emission processes or not? And thus I should mention that this autoemission process occurs at the critical parameters. We were investigating the maximum current of this pattern, so we applied the huge voltage. And at the voltage about 800 V the emission current fall down abruptly. That means that all the tubes have been “burned”, as we called it.

Perhaps, carbon nanotubes degradation is the main reason of emitting nanotubes quantity permanent changing and hence a big noise.

The degradation problem solving is connecting with its mechanism. To be exact, it is necessary to reduce control voltage in order to decrease strains that are exists in the nanotubes and catalyst connecting area. Therefore, we had to reduce the autoemission threshold voltage, but this is solving technologically.

Conclusions.

Two main problems (emission current noises and degradation) that were revealed during this work are related with technical realization. And the way to solve these problems is to improve technical equipment and control the process from the beginning to the end.

The experiments that were held during this work helped to formulate requirements specification for more complete pilot type plant manufacturing for carbon nanotubes growth. Such plant have already been produced and passing the tests on the manufacturer at the present. It is providing next possibilities in this plant: oilless vacuum eviction to the pressures of $\sim 10^{-6}$ mercury millimeters, controlling of nanotubes growth direction, HF and UHF plasma with high homogeneity.