Nanodiamond composite as a material for cold electron emitters

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Abstract. Characteristics of field-induced electron emission were investigated for one of newly designed all-carbon materials – nanodiamond composite (NDC). The composite is comprised by 4..6 nm diamond grains covered with 0.2..1 nm-thick graphite-like shells that merge at grain junctions and determine such properties as mechanical strength and high electric conductivity. Large number of uniformly distributed sp³-sp² interfaces allowed to expect enhanced electron emission in electric field. Combination of these features makes NDC a promising material for cold electron emitters in various applications. Experimental testing confirmed high efficiency of electron emission from NDC. In comparison with previously tested forms of nanocarbon, NDC emitters demonstrated better stability and tolerance to performance conditions. Unusual activation scenarios and thermal dependencies of emission characteristics observed in experiments with NDC can add new background for explanation of facilitated electron emission from nanocarbons with relatively “smooth” surface morphology.

1. Motivation
Carbon nanostructures are generally considered as one of the most promising solutions of the problem of cold electron emitters for vacuum and plasma-filled devices. Chemical inertness of carbon allows to expect from nanocarbon emitters stability, tolerance to performance conditions and long lifetimes. Yet, the practical experience presently accumulated with nanotube-based and other structures utilizing geometric enhancement of electric field at high-aspect-ratio surface elements demonstrates that emission stability remains one of primary obstacles for their wider commercial applications. Degradation of these materials can be associated with very strong electric field focused at small-area active emission spots. At the same time, various species of carbon nanostructures with much smoother surface morphology are also known as efficient electron emitters [1]-[7]. They are studied much less comprehensively than nanotubes, both by theory and experiment, and even the actual mechanism of facilitated emission remains unclear in many cases. But, due to presumably lower field values at emitting areas, these low-aspect-ratio nanocarbons could eventually give a basis for construction of emitter with better durability.

The presented work was aimed to: 1) test electron emission properties of a new nanocarbon material with low field enhancement factor and 2) provide new experimental data on fundamental emission mechanisms realized with materials of this type.
2. Nanodiamond composite (NDC)

The form of nanocarbon investigated in this work – nanodiamond composite (NDC) [8]-[10] – represents a derivative of ultra-dispersed (4-6 nm) diamond powder. By CVD process, nanodiamond grains were covered with 0.2-1 nm-thick graphite-like shells merging at junctions to form a solid matrix binding the grains together. Despite high porosity (30-60% vol.), the composite is characterized by good mechanical properties – for instance, microhardness between 2 and 7 GPa. The graphite-like matrix determines relatively high electric conductance (~kOhm·cm at room temperature). Detailed investigation revealed semiconductive type of conductance with activation energy 0.05-0.2 eV and Hall constant very close to 0.

Prior to our study, no data on emission properties of NDC were available, but its structure allows to expect enhanced emission efficiency. Active emission sites at low-aspect-ratio nanocarbons are often associated with sp³-sp² phase junctions ([2], [4]), and density of such junctions at NDC surface is very high. In addition, NDC presumably possesses other features that can determine cold cathodes’ quality:

- Its surface structure can be controlled via thermal and field treatment. Initially, graphene shells are relatively low-defect, thus the surface must be stable at room temperature. To allow its field-induced reconstruction (a normal procedure for many nanocarbon emitter – see, for instance, in [5]), we can heat the sample to high temperature to cause graphitization process in diamond grains, which can involve some of shell atoms and increasing surface mobility.
- Mechanical sturdiness is vital to withstand destructive effects of electric forces, sputtering, etc.
- High electric conductance through uniformly distributed sp²-phase “network” practically excludes ohmic losses in sample volume.
- Substantial thermal conductivity can also be important for high-current applications.

3. Experimental layout and procedures

Experiments were performed in a vacuum chamber at (1-3)·10⁻⁷ Torr residual gas pressure. NDC samples with 0.02-3 cm² emitting surface area were placed in 2 mm-wide planar gap formed by smooth cap electrodes (figure 1). Emission current was measured with a current probe set opposite the sample. To control emission activity of the sample, different field- and/or thermal treatment procedures were tested, consisting in simultaneous or alternate heating of the sample to temperatures 100-900ºC and extraction of different current levels between 1 nA and 1 μA.

![Figure 1. Experimental layout.](image)

4. Experimental results and discussion

“Fresh” samples in as-produced state explainably demonstrated low emission activity (curve 1 in figure 2). Different thermo-field treatment procedures were tested to increase their current yield. The most effective routine included 3 steps:

- Heating of the sample to approximately 800ºC;
- application of electric field sufficient for extraction of 0.1-1 μA current from hot sample;
- gradual sample cooling down to room temperature with continued extraction of current.

Characteristics of NDC in the state of the best achieved activation were typical for low-aspect-ratio carbon emitters. Threshold current 1 nA appeared at 5 kV voltage applied across the gap (curve 3 in figure 2), i.e. at 2.5 kV/mm average field. The I-V curve plotted in Fowler-Nordheim (FN) coordinates (6 in figure 3) gives a linear trend with slope angle formally corresponding to:
Figure 2. I-V plots for a 0.02 cm² NDC sample at different stages of thermo-field (TF) treatment test program.

- field enhancement factor $\beta=2700$, if work function $W=4.5$ eV is assumed, or
- $W=0.5$ eV for more realistic estimate $\beta=100$.

Special high-current tests were not performed due to technical complications. Maximum observed current 13 $\mu$A was attained from 0.02 cm² sample at 12 kV voltage, which corresponds to 6 kV/mm mean field and 0.65 mA/cm² average current density.

In comparison with carbon emitters studied in our previous experiments [6],[7], NDC demonstrated much better sturdiness. In the course of testing of treatment procedures, NDC samples withstood multiple cycles of activation followed by intentional de-activation, heating to 900°C, discharges, etc., but their ability to produce current wasn’t exhausted, and no visible changes of surface were noted.

In a few cases, the measured current characteristics demonstrated unusual features that can give useful clues to explanation of the phenomenon of facilitated emission from NDC and other multi-phase nanocarbons. One of them concerns transformation of I-V plots with sample activation, illustrated in figure 3. According to the basic theory, plots of field-induced current in FN coordinates can be approximated by straight lines with slope angles proportional to $W^{3/2}/\beta$. Emitter activation presumably consists in reduction of work function and/or increase of field enhancement factor. So we can expect FN plots to remain straight lines while gradually shifting up and reducing the slope angle.

In experiments with NDC, activation scenario was different:
- at first (curves 1,2 in figure 3), we observe parallel displacement of the characteristics, as though effective emitting area grows while all other parameters are conserved;
- then (curves 3-5), the plot breaks in two straight links: an interval with much lower slope appears at the high-voltage end of the curve and gradually expands to lower voltages;
- the low-slope link occupies (almost) all the plot (curve 6).

In principle, current saturation due to poor conductance in the sample or space-charge field of emitted electrons in vacuum are well-known phenomena. Yet, both these explanations are quantitatively inapplicable to the case of low-ohmic NDC, considering that the FN plot bending was observed for emission currents as low as 10-100 nA.

Transformation of I-V curves with temperature also followed an interesting scenario. At room temperature, FN characteristics for moderately activated NDC samples were linear and self-reproduced in repeated measurements (figure 4a). Plots measured at increased temperatures remained linear, but had steeper slope. Alteration of I-V characteristics occurred no sooner than a certain level of current was reached (figure 4b), thus a kind of thermal hysteresis was observed. When the sample
Figure 4. Transformation of FN plots with temperature. Emitter activation degree approximately corresponds to curve 2 in figure 3. Arrows mark starting points and order of data acquisition.

temperature was returned to ambient level, the I-V curve returned to its “proper” position only after extraction of relatively high current (figure 4c). The hysteresis was observed even when as much as a few days passed between sample heating and emission measurements. The latter observation means that it cannot associated with accumulation and removal of surface contaminants from residual gas (which would take much shorter time), but rather with deeper reconstruction of emitter structure, temperature-specific and occurring only when substantial current is extracted.

5. Conclusions
In accordance with expectations, NDC samples demonstrated good (but not outstanding) efficiency of field-induced electron emission (1 μA current yield in 5-7 kV/mm average field), sturdiness and tolerance to operation conditions. As for many other species of nanocarbon with low geometric field enhancement, such factors as temperature, electric field and extracted current have long-time complex effects on emission characteristics of NDC, which allows to achieve emission activation via thermo-field treatment procedures.

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