Carbon Nanotube Emitters in Sensoric Application

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***Abstract*—A contemporary approach to study the emission properties of carbon nanotubes (CNTs) in low distances between two electrodes is described in this paper. The method could be used in modern MEMS pressure sensor applications. The field emission works on the principle that the field emission current is correlated with the electrical field intensity, i.e., the anode-emitter distance when the applied voltage is fixed. This means that the CNTs array serves as the emitter source of electrons between the cathode and the anode in the electric field. The measurement of emission current density flowing through the electrodes is carried out in a vacuum chamber pumped by a turbomolecular pump. The vacuum chamber is equipped with a linear nano-motion drive SmarAct that enables precise changes of the distance between two electrodes inside the vacuum chamber (step width from 50 nm to 1000 nm, sub-nanometer resolution). For this experiment, CNTs are deposited using a thermal chemical vapour deposition.**

Keywords-carbon nanotubes; emission properies; thermal chemical vapour deposition; microwave torch deposition.

I. INTRODUCTION

Carbon nanotubes (CNTs) are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, and have remarkable electronic properties and many other unique characteristics. The diameter of a nanotube is on the order of a few nanometers (approximately 50 000 times smaller than the width of a human hair), while they can be up to several millimeters in length [1] [2]. For these reasons, they have attracted huge academic and industrial interest, with thousands of papers on nanotubes being published every year.

Field emission involves the extraction of electrons from a solid by tunnelling through the surface potential barrier. The emitted current depends directly on the local electric field at the emitting surface E, and on its work function, ϕ. Fowler-Nordheim model [3] shows that the dependence of the emitted current on the local electric field E and the work function ϕ, is exponential like. As a consequence, a small variation of the slope or surrounding of the emitter and/or the chemical state of the surface has a strong impact on the emitted current. The small diameter of carbon nanotubes is very favourable for field emission. The device emits electrons when an electric field or voltage is applied [4] [5].

Several techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide and chemical vapour deposition (CVD). Most of these processes take place in vacuum or with process gases. Large quantities of nanotubes can be synthesized by CVD methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable [6-8].

This paper is structured as follows: The field emission mechanism is described in Section II. In Section III, we describe the sample preparation and measurement setup. A short discussion about the obtained results and the method for possible packaging of emission pressure sensor is described in Section IV. Section V concludes the paper.

II. THEORY - EMISSION MECHANISM

Large field amplification factor, arising from the small radius of curvature of the nanotube tips, is partly responsible for the good emission characteristics. It is however still unclear whether the sharpness of the nanotubes is their only advantage over other emitters, or if intrinsic properties also influence the emission performances.

If the nanotubes seem to follow the Fowler-Nordheim law, they can be thought of as metallic emitters. Nanotube emissions deviate from Fowler-Nordheim model. Such deviations are usually attributed to space-charge effects, which induce a diminution of the F-N slope at high fields. Thus nanotubes cannot be considered as usual metallic emitters [3].

Theory of emission mechanism is shown in Fig. 1. Field emission involves the extraction of electrons from a solid by tunnelling through the surface potential barrier. The emitted current (I_E) depends directly on the local electric field at the emitting surface E, and on its work function, ϕ. If the applied voltage is fixed, the emitted current depends directly on emitter distance x. The variable E_F represents Fermi level.

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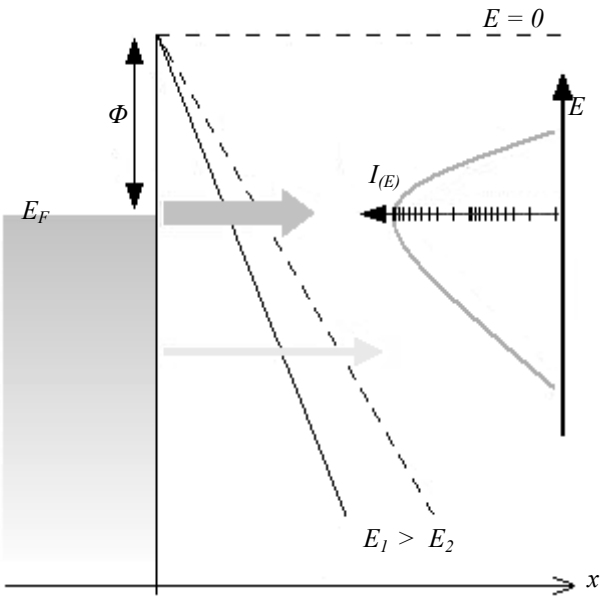

Figure 1. Theory of emission mechanism (Fowler-Nordheim law) [3]

Also, for nanotubes, electrons are not emitted from a metallic continuum as in usual metallic emitters, but rather from well-defined energy levels of ~0.3 eV half width corresponding to localized states at the tip. The energy spread of nanotubes is typically half of the metallic emitters (~0.2). The shape of the energy distribution suggests that the electrons are emitted from narrow energy levels. The greatest part of the emitted current comes from occupied states with a large density of states near the Fermi level, but the other deeper levels also contribute to the field emission. The position of these levels with respect to the Fermi level, which depends primarily on the tip geometry (i.e., tube chirality, diameter and the eventual presence of defects), would be, together with the tip radius the major factors that determine the field emission properties of the tube. Finally, it is worth noting that the presence of localized states influences the emission behaviour greatly. Local density of states at the tip reaches values at least 30 times higher than in the cylindrical part of tube increasing the carrier density for strong emission.

III. EXPERIMENTAL

A contemporary approach to study the emission properties of carbon nanotubes in low distances between two electrodes was used in this paper. Each electrode consists of high doped silicon substrate. The field emission works on the principle that the field emission current is correlated with the electrical field intensity, i.e., the anode-emitter distance when the applied voltage is fixed. This means that the CNTs array serves as the emitter source of electrons between the cathode and the anode in the electric field. The measurements were five times repeated and the same results were obtained.

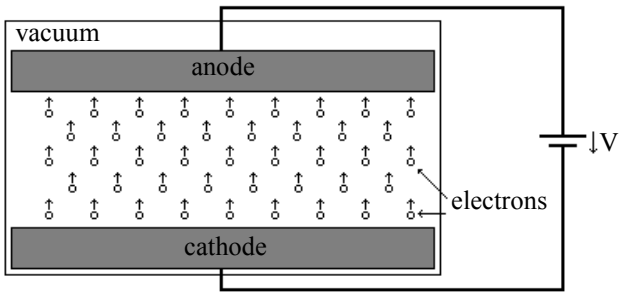

Figure 2. Schematic illustration and principle of measuring the emission properties.

The measurement of emission current density flowing through the electrodes was carried out in a chamber pumped by a turbomolecular pump and equipped with feedthroughs for voltage application and current measurement. The vacuum chamber was equipped with a new vacuum compatible linear nano-motion drive SmarAct that enables precise changes of the distance between two electrodes inside the vacuum chamber (step width from 50 nm to 1000 nm, sub-nanometer resolution). Special software, enabling to set up the step size, number of the steps and speed of the motion, was developed for its control. Additionally, a measurement control unit and the software were prepared for an automatic electrical measurement.

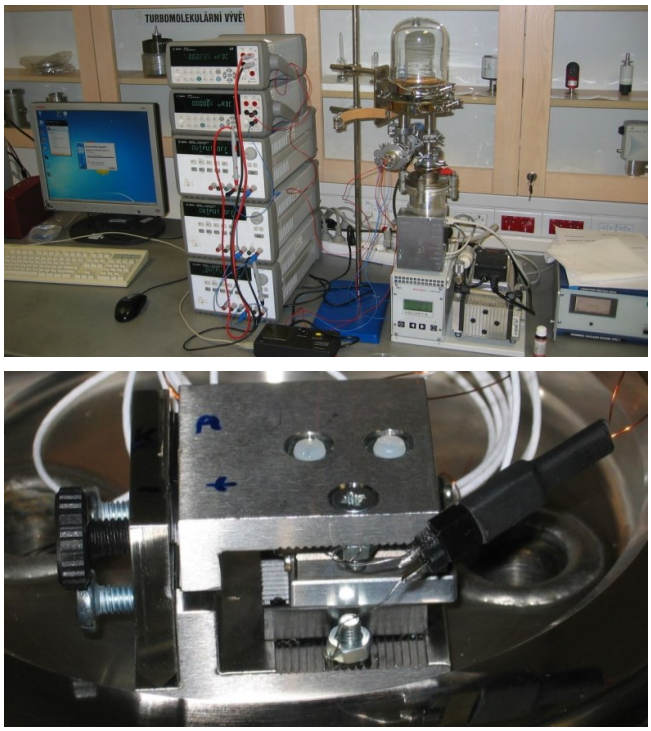

Figure 3. The workplace for emission measuring (up) and the detail of nano-motion drive SmarAct (down).

Electrode substrates on silicon wafer were fabricated using lithography and standard thin-film technology. The base for silicon electrodes is monocrystalline N-type 4” Si wafer with <100> orientation and the thickness of 525 μm (ON Semiconductor). Wafer is doped with antimony and its

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resistivity is 0.005 Ω.cm. On the places where the MWCNTs should grow, the 300 nm thick layer of Ti/Ta were sputtered to ensure better adhesion of lately deposited MWCNTs. Then on the tantalum layer was evaporated 5 nm thick catalyst layer of iron. Prepared substrates were then cut to separate microelectrodes and used as the substrate for grown of vertically aligned MWCNTs.

For this experiment, carbon nanotubes were deposited using a thermal chemical vapour deposition. Typical deposition process was as follows. The substrate was placed in quartz boat and put in the centre of horizontal furnace equipped with quartz glass tube (1000 mm long) terminated with flanges as it is schematically shown in the Fig. 4.

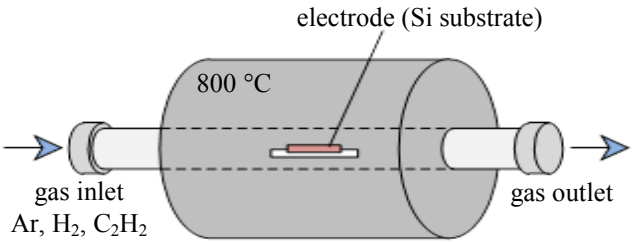

Figure 4. Scheme of thermal CVD furnace.

Gas flow rates were controlled by electronic flow controllers. The inner diameter of quartz glass tube is 45 mm and hot zone length is 150 mm. The furnace deposition temperature was measured by K type thermocouple. The substrate was heated under mixture of Ar, flow rate 2800 sccm, and H_2, flow rate 500 sccm, to 800 °C with ramp rate of 25 °C.min^{-1}. The CNTs were grown at 800 °C under mixture of Ar (1400 sccm) and C_2H_2 (30 sccm). Deposition time was 20 minutes. After the deposition the substrate cooled down under Ar flow (1400 sccm). A detailed study of the deposition of CNTs and their characterization were published in [9] [10].

IV. RESULTS AND DISCUSSION

Successfully fabricated electrodes with deposited MWCNTs were analysed optically using SEM (TESCAN, Czech Republic). SEM micrographs of fabricated electrode with different scale are shown in Fig. 5.

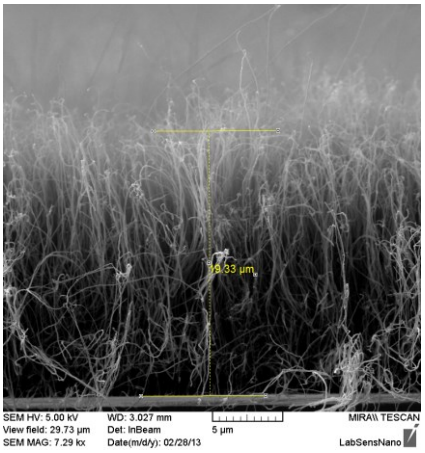

Figure 5. SEM analysis of the CNTs.

Measurements were performed at pressure of 10^{-4} Pa for ten electrode distances – from 84 µm to 100 µm. For these ten distances, the same results were obtained for multiple times. The emission current in dependence on the applied voltage was measures as basic results. Graphs of these dependences are shown in Figs. 6 and 7.

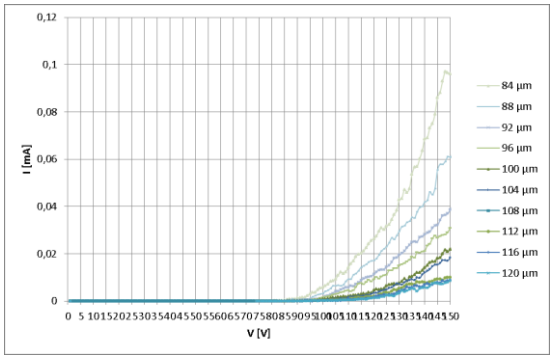

Figure 6. Result of measured emission current in dependence on the applied voltage.

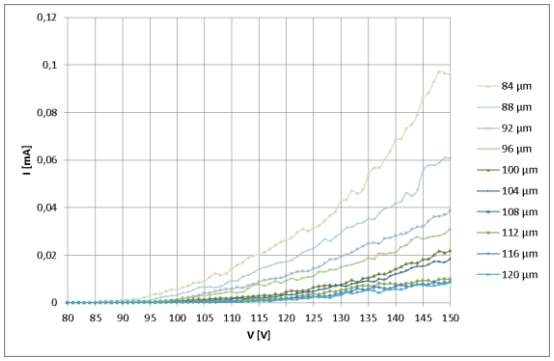

Figure 7. The detail result of measured emission current in dependence on the applied voltage for higher voltages.

In the set of experiments on the array with CNTs with dimension of 4x4mm, the field emission results show that in the small electrode distance, there is the low turn-on field (smaller than 1 V/µm) and there is achieved a high current density at 1,8 V/µm.

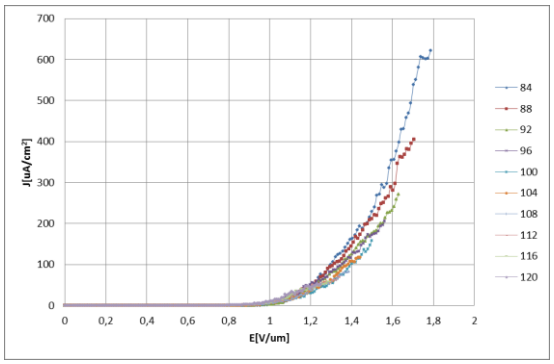

Figure 8. Results of current density in dependence on intensity for ten electrode distances.

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The measured results follow the Fowler-Nordheim law as expected. For smaller electrode distances, it is expected a higher current density for same applied voltages or vice versa, the same current density at lower applied voltages.

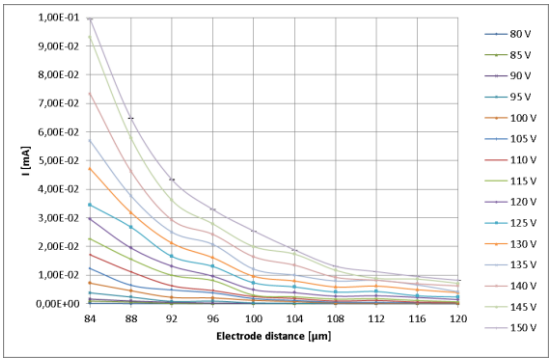

Figure 9. Results of emission current in dependence on the electrode distance for applied voltage from 80 to 150 V.

The curves in Fig. 9 show, that the emission current depends on electrode distance when the applied voltage is fixed. This could be a confirmation of the proposed solution and CNTs could be used as emitters in a pressure sensor.

A method for packaging emission pressure sensor was also invented so the emission could exist outside the laboratory vacuum chamber. The entire sensor could be encapsulated in the housing known from the production of vacuum tubes (Fig. 10).

Figure 10. Possible package for emitter made from carbon nanotubes.

Two conductive silicon electrodes are bonded together. The cathode is with carbon nanotubes, the anode is flexible. The pressure from external inlet causes the bend of anode, i.e., the emission current (electrode distance) is changing when the applied voltage is fixed.

The zirconium getter should be inside the tube to maintain vacuum for long-term activities. Getter is used for disposal of residual gases and mainly for moisture absorption.

V. CONCLUSION

In conclusion, we successfully fabricated vertically aligned carbon nanotubes using CVD method. The tips of nanotubes serve the electrons. The emission current is dependent on electrode distance. The measured dependencies show that the CNTs are stable and low noise. If one of the electrodes will be flexible (membrane), this system could be used for pressure sensing. We also introduced the method for packaging emission pressure sensor for application outside the laboratory vacuum chamber.

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