PERSPECTIVE CARBON MATERIALS AS ELECTRON EMITTERS

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Abstract

Carbon materials are good candidates as electron emitters. In this article will be described emission properties of carbon nanotubes prepared by chemical vapour deposition (CVD). The measurement of emission current density flowing through the electrodes will be carried out in a vacuum chamber pumped by a turbomolecular pump. The vacuum chamber will be 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). The measured results will be compared with Fowler-Nordheim theory. One of the proposed solutions for usage CNTs as emitters is in a pressure sensor. A method for packaging emission pressure sensor will be also invented so the emission could exist outside the laboratory vacuum chamber. The electrodes of the sensor could be bonded using glass frit bonding or anodic bonding technology.

Keywords: Carbon nanotubes; emission properties; thermal chemical vapour deposition; anodic bonding

1. INTRODUCTION

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces, more specifically, pi-stacking [1].

Nanotubes have been constructed with length-to-diameter ratio significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials [2].

Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp2 bonds, similar to those of graphite. These bonds, which are stronger than the sp3 bonds found in alkanes and diamond, provide nanotubes with their unique strength.

For these reasons, they have attracted huge academic and industrial interest, with thousands of papers on nanotubes being published every year.
2. EMISSION MECHANISM

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, $\phi$. Fowler-Nordheim model [3] shows that the dependence of the emitted current on the local electric field $E$ and the work function $\phi$, 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].

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, $\phi$. If the applied voltage is fixed, the emitted current depends directly on emitter distance $x$. The variable $E_F$ represents Fermi level.

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.

3. EXPERIMENTAL

For this experiment, carbon nanotubes were deposited using a thermal chemical vapour deposition [6-8]. 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. 2 (left).
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$_2$H$_2$ (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].

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).

**RESULTS AND DISCUSSION**

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. In the set of experiments on the array with CNTs with dimension of 4x4 mm, the field emission results (Fig. 4 left) 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.
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.

The curves in Fig. 4 (right) 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.

![Fig. 4 Results of current density in dependence on intensity for ten electrode distances (left) and results of emission current in dependence on the electrode distance for applied voltage from 80 to 150 V (right).](image)

If one of the electrodes will be flexible (membrane), this system could be used for pressure sensing. 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.

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 using glass frit bonding. This technology is widely used in industrial microsystems applications where fully processed silicon wafers have to be bonded. The first successfully attempts are shown in Fig. 5.

![Fig. 5 Cross section of glass frit bonding](image)
This end-of-process-line bonding must fulfill some very specific requirements, such as: process temperature limited to 450 °C to prevent any temperature-related damage to wafers, no aggressive cleaning to avoid metal corrosion, high process yield since wafer processing to this stage is expensive, bonding of wafers with certain surface roughness or even surface steps resulting from metal lines electrically running at the bonding interface to enable electrical connections into the cavity sealed by the bonding, as well as a mechanically strong, hermetically sealed, reliable bond. All of these requirements are fulfilled by the glass frit bonding process, which additionally can be very universally applied since it can be used to bond almost all surfaces common in microelectronics and microsystem technologies.

5. 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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