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Electron emission from Spindt-like carbon nanotubes field emission cathodes (FECs)

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We present field emission characteristics from Spindt-like carbon nanotubes (CNT) films obtained in a two steps method. The two steps method was elaborated in Tele & Radio Research Institute (Poland) and it consists of two independent processes: first, the physical vapour deposition (PVD) process in which a nanocomposite film built of Ni nanocrystals and carbonaceous matrix is prepared; second, the chemical vapour deposition (CVD) process in which the nanocomposite film is modified in high temperature (650 °C) and in atmosphere of hydrocarbons. A field emission property of CNT films is measured using a diode type system. Emission current versus applied field (I–V) is characterized by varying potential from 0 to 4 kV. The results show that emission current and threshold voltage are depended on CNT films morphology and topography – the factors about which technological parameters decide.

Keywords: carbon nanotubes, physical vapour deposition (PVD), chemical vapour deposition (CVD).

1. Introduction

Field emission cathodes (FEC) similar to those of the Spindt type have been developed for more than two decades [1]. Many types of cold cathodes using many types of carbonaceous materials such as carbon nanotubes, carbon fibers, coated or nanostructured diamond and graphite nanopowders have been used for field emitters, but the electric fields required by all of these materials for producing useful current densities remain too high to be sustainable in many high power devices. Carbon nanotubes (CNTs) are helical tubes with diameters ranging from about 2 to 100 nm and lengths of several micrometers.

The development of flat panel displays and scanning microscope probes has shown that CNTs can give very high local current densities of about few hundreds amperes per cm^2 and that large enhancements of the applied electric field of more than 1000 are possible [2].

Many different constructions of cathodes have been proposed (diode- or triode-type emitter structures). The triode structure is similar to the Spindt type FEC [1], but has a larger gate hole diameter due to excellent field-emission characteristics of CNTs. CNT emitter is proposed as a set of dots formed inside gate holes (by, *e.g.*, screen

printing of a photosensitive paste containing CNTs and subsequent back side exposure of an UV light [3]).

In this paper, we present FEC prepared by a two steps method and composed of single, separated CNTs placed in a structure that could play a role of a gate. Such set FEC and mentioned structure are dispersed on a surface of a substrate covered with a film with multiphase structure. It was found that field emission from these FECs depends on CNTs properties and their position in a gate and film-matrix. We called these FECs films Spindt-like FECs films.

2. Experiment

Spindt-like FECs containing multi-walled carbon nanotubes (MWCNTs) were prepared by a two steps method elaborated in Tele & Radio Research Institute. In the first step of this method, the physical vapour deposition (PVD) process was applied. The evaporation of fullerene and nickel acetate in the PVD chamber was carried out from two separated sources under a dynamic vacuum of 2×10^{-5} mbar. The content of Ni in the PVD samples was determined by the atomic absorption spectroscopy (AAS) method. In Table 1, the parameters of PVD processes as well as Ni content in films are presented.

T a b l e 1. PVD process parameters (I_{C60} – current intensity of C_{60} source, I_{Ni} – current intensity of Ni source, t – process duration time).

Sample number	I_{C60} [A]	I_{Ni} [A]	Substrate	t [min]	Ni content [wt%]
S1PVD	1.9	1.25	Si, *n*-type, ⟨111⟩	60	50.00
S2PVD	2.1	1.10	Si, *n*-type, ⟨100⟩	30	16.43

In the second step, PVD-films were modified by the chemical vapour deposition (CVD) method with xylene gas as a modification factor. The CVD reactor which consisted of a 3 cm diameter quartz tube was placed in a furnace with two heating zones. Xylene was evaporated in the first zone at the temperature of 180 °C. In the second zone (at the temperature of 650 °C), where PVD films were placed, xylene was decomposed and condensed on these samples. Xylene was transported to this zone by argon flow. Due to CVD process, CNTs growth on the PVD-films was realized.

Technological parameters of CVD process are presented in Tab. 2.

T a b l e 2. CVD processes parameters (T – temperature of second zone, t – process duration time, F_{Xy} – xylene flow rate, F_{Ar} – argon flow rate).

Sample number	T [°C]	t [min]	F_{Xy} [ml/min]	F_{Ar} [l/h]
S1CVD	650	30	0.1	40
S2CVD	650	10	0.1	40

SEM studies of prepared in both steps samples were performed with the scanning electron microscopy (SEM) method. SEM investigation was performed with the JEOL JSM-7600F field emission scanning electron microscope operating at 5 keV incident energy. Both secondary (SE) and backscattered (BS) electrons detection were applied for imaging the film.

AFM measurements were done with the EXPLORER 2000 microscope with a standard Si_3N_4 cantilever in a contact mode.

U–I characteristics were measured in a diode system where CVD-film was a cathode and anode was a spherical shape tip. All measurements were performed at dynamic vacuum (from 2×10^{-6} to 6×10^{-6} mbar). Applied voltage was 0 to 4 kV and the distance *d* between anode and cathode could be changed (in our case from 170 μm to 400 μm).

3. Results and discussion

PVD process films (with thickness in the range of 200–300 nm) deposited on Si wafers were obtained. These PVD films are composed of a carbonaceous matrix (amorphous carbon) and nickel nanograins, what was found as a result of earlier X-ray diffraction studies.

In Figures 1**a** and 1**b** SEM images of samples S1PVD and S2PVD are presented. The surface of both samples is covered with carbon nanograins. Grains covering S1PVD sample surface are of diameters between 150–300 nm and their shape was prism-like. Our studies of back scattered electron images have shown that these grains could be mostly carbonaceous objects (Fig. 1**b**). The surface of sample S2PVD was

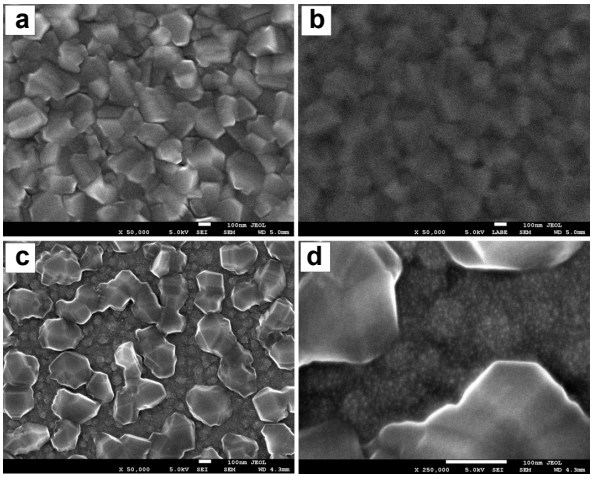

Fig. 1. SEM images of S1PVD SEI mode (**a)**, S1PVD – low angle backscattered electron image mode (LABE) (**b**), S2PVD – SEI mode (**c**, **d**).

covered with two kinds of grains: one grain was like in sample S1PVD; second kind of grains had smaller diameters (few tens of nm) and they were placed under these bigger one.

These small grains were composed of many very small grains with a size of few nanometers (Figs. 1**c** and 1**d**).

Longer process duration time on the PVD films is connected with a covering of all surface of a sample with carbon grains (prism-like). We have found that sources volume is too small to place enough nickel acetate powder (that evaporation rate is high) to realize the process in one hour. Then, we have obtained a two-layered film where the bottom layer is richer with Ni and the top layer is free of Ni.

After modification in CVD process PVD films, we have found on the surface of samples S1CVD and S2CVD many objects such as: individual carbon nanotubes, carbon-rich grains, Ni nanograins and nanoporous islands. SEM images of obtained

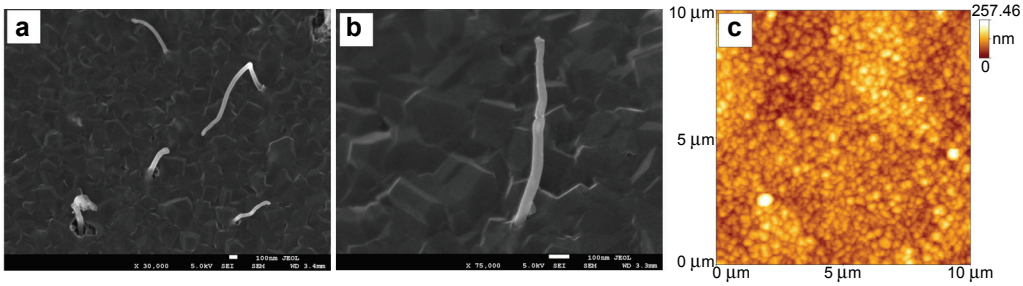

Fig. 2. SEM (**a**, **b**) and AFM (**c**) images of Spindt-like CNT film type 1 – hill-like structures with single CNTs.

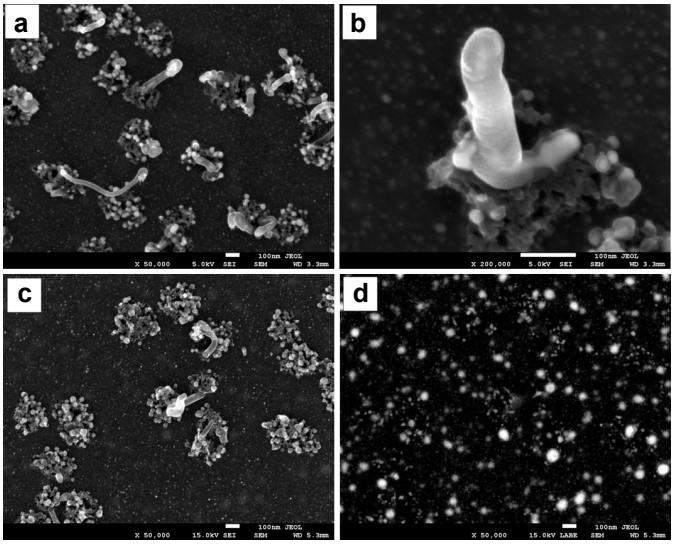

Fig. 3. Images of Spindt-like CNT film type 2 – flat structure with single CNTs: secondary electron images (SEI) (**a**, **b**, **c**), low angle backscattered electron (LABE) image (**d**).

film forms are presented in Figs. 2**a**, 2**b** and Figs. 3**a**, 3**b**. In the case of both samples, a characteristic topography based on a flat structure with single CNTs embedded in hill-like structures was observed. The whole structure has a Spindt-like character.

Shown in Figs. 2**a**, 2**b**, the surface of S1CVD sample reflects the surface of S1PVD sample but from this film CNTs sprout with a distance between them of ~1 μm. Found in backscattered electron images, nickel nanograins are dispersed within the film with high density but not always they are precursors for CNT growth. The length of observed CNTs is few hundreds nm and their axes are inclined from the vertical by a few degrees. In Figure 2**c**, AFM image of this sample is also shown. Due to a repulsion effect between AFM tip and nanotubes, CNTs are not clearly visible in the obtained images. We suppose that bright objects (with a high ~250 nm) protruding from the film surface could be a single CNT. The area connected to these bright objects is much bigger, and a single CNT diameter is enlarged due to a repulsion effect between a long (~1 μm) and AFM scanning tip. The measured roughness for this sample was 15–27 nm.

The surface of S2CVD sample (Figs. 3**a**, 3**b**) is almost flat between single CNTs protruding from porous islands. The length of observed CNTs is between 100 and 300 μm and the distances between them can be compared with their length. Nanograins of nickel are not visible on SEM image, but while analyzing BS images, it is clear that they are dispersed in the whole film volume and their diameters are up to few tens of nanometers. Some Ni nanograins become precursors for CNT growth in CVD process.

4. Field emission

Electron emission characteristics (*I–U* plots) for these films are presented in Fig. 4. *I–U* plots were measured for different anode–cathode distances, but the most stable

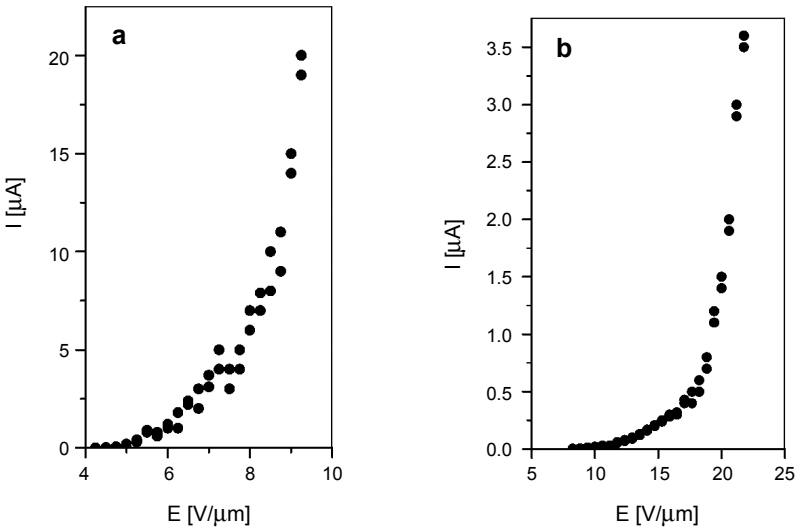

Fig. 4. *I–U* plot for sample: S1CVD (**a**), and S2CVD (**b**).

emission was observed for distances bigger than 300 nm for sample S1CVD and 150 nm for sample S2CVD. Taking into account the fact that nanotubes for sample S1CVD were longer than these found in sample S2CVD, this effect could be interpreted as a result of CNT length. We have also found that in both cases, the emission is stable for more than 10 hours.

The emission current of the sample S1CVD was about 10 times higher than for the sample S2CVD (at electric field 10 V/μm). This effect could be connected to a lower density of CNTs placement on a S1CVD film surface than in S2CVD sample. It was also observed that electron emission started at a lower value of the electric field for sample S1CVD. This low threshold value could be attributed as well to a distribution density of CNTs as to the length of CNTs. These both factors have an influence on an electric field shape in the vicinity of the sample surface and could cause a lowering of the potential barrier for extracted electrons.

5. Conclusions

We can conclude that the dispersion and length of CNTs grown in our two steps method strongly influence the electron emission from obtained films with a Spindt-like structure on the surface. It was found that electron emission current intensity increases when the CNTs distribution density is about one CNT on 1 μm^2 and CNTs length is few hundreds of nanometers.

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