Optimization of Silicon Field Emission Devices by the Addition of Carbon Nanotubes

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Abstract

This work relates the fabrication and characterization of silicon field emission devices coated by carbon nanotubes (CNTs). The Si field emitters (microtips) were fabricated by the well-established HI-PS technique, while CNTs were deposited over these emitters by the cost-effective electrophoretic deposition process. Our results show a considerable improvement of electron emission characteristics for devices with CNTs coating, presenting a reduction of macroscopic electrical field about thirty five times in comparison with devices without CNTs. The association of Si tips with carbon nanotubes is very promising for the development of field emission devices with optimized characteristics and miniaturized gas ionization sensors, which work with low voltage.

Keywords: Field Emission, Si microtips, HI-PS technique, Carbon Nanotubes (CNTs)

Introduction

The field emission phenomenon is based on physical tunneling quantum effect (described successfully by Fowler and Nordheim in 1928 [1]), where electrons are extracted from a material through the surface potential barrier by applying a strong electric field. The obtaining of elevated emission is related mainly to nature of materials that compose the emitters (cathodes) and their geometrical shape (sharp structures increase the electrical field at their apex), which need less energy to promote electron emission [2]. Thus, the development of efficient field emission devices (FE) requires the use of materials with relative low work function composed by geometric structures with sharp aspect (conical tips shape are usually preferred).

The notable interest in development of devices based on field emission phenomenon is due to their possible applications in flat panel displays, high frequency devices, vacuum microelectronic devices, instrumentation based on electron beam and highly sensitive sensors, because these devices can emit electrons at room temperature with low voltage applied, being used in the applications mentioned as ionization sources (also known as cold cathodes) [3].

Carbon nanotubes (CNTs) are promising as new nanomaterial for sensors development as also they are potential candidates for field emission applications. Advantages of CNTs over other materials are its high surface volume ratio, small dimension, high strength, good electrical conductivity and high thermal conductivity. In addition to these properties, they have remarkable characteristics as high aspect ratio, good chemical stability, sharp tip structure and low work function [4].

Moreover, the use of silicon (Si) for the development of field emission devices is very attractive because of the possibility of enjoying consolidated microfabrication processes for obtaining microtips, which are efficient structures to make the cold cathodes, to the conventional microelectronic circuits, enabling the manufacture of compact and portable equipments.

However, in the search of obtain better performance in the process of electron emission, Si microtips can be coated with materials of low work function, since these materials does not affect too much the geometric aspect of electron emitters.

In this context, the objective of this work is to evaluate the response of field emission devices composed by arrays of Si microtips coated with carbon nanotubes in order to obtain devices with enhanced efficiency of electron emission to be applied as gas sensor in the future, through the ionization of gases at low voltages into miniaturized devices [5].

Experimental Procedure

Si FE devices were obtained by the well-established HI-PS (Hydrogen Implantation – Porous Silicon) technique [6], and afterwards they were covered by multi-walled carbon nanotubes (MWNTC) by electrophoresis process.

Si FE devices fabrication

Arrays of 2500 silicon microtips, enclosed in an area of 3x3 mm^2, were obtained by HI-PS MEMS fabrication process [6-8] to be applied as cold cathodes for field emission. The staring materials were p type silicon substrates with 10 Ωcm of resistivity and <100> orientation.

Masks with circular geometries with diameter of 25 μm allowed the obtaining of Si microtips with height and apex around 10 μm and 150 nm respectively, without structural improvement process steps [8] as shown in Figure 1 (Figure 4a shows a single Si tip image). The detailed process of fabrication of silicon microstructures was reported elsewhere [7,8]. Ohmic aluminum contact was made on backside of the Si substrates.

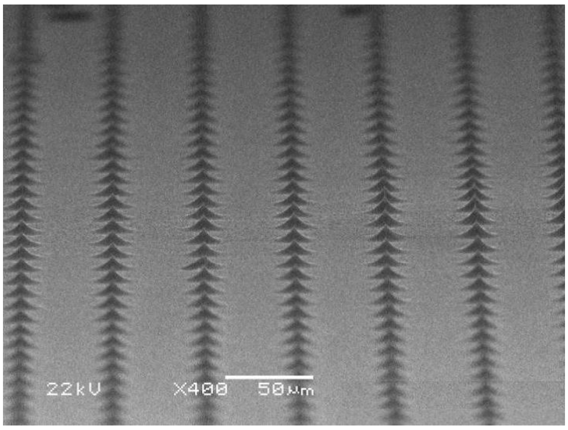


Figure 1: SEM images of fabricated Si FE device. Overall aspect of the Si microtips array [8].

MWCNT Electrophoretic Deposition

Electrophoretic deposition (EPD) was the method employed in this work to cover Si microtips with multi-walled carbon nanotubes (MWCNTs). EPD is a cost-effective method commonly used in the processing of ceramics, coating and composite materials [9, 10], as well as electrode coatings. EPD is efficient and useful for depositing thin and thick films of CNTs on conductive surfaces [11-13]. However, to realize the process of electrophoresis, carbon nanotubes must be dispersed in aqueous solution and conditioned properly (chemically functionalized).

In this work, MWCNTs were functionalized as described previously in [14] and, before the EPD process, the solution was sonicated for 2 hours. Then, MWCNTs dispersed in the solvent were deposited on the micromachined silicon surface under an applied electric field between the cathode (silicon) and the anode (stainless steel) at room temperature. All EPD processes were made with a small electrolytic cell, filled with 1 cm^3 of MWCNT solution, and the distance between the electrodes was kept constant (1 cm), as represented in Figure 2.

EPD process was carried out with a Source and Measurement Unit (SMU) Keithley, model 236, controlled by Virtual Instrumentation with LabVIEW Software (National Instruments, TX). The applied current was 2 mA during 20 minutes. After EPD, samples were left to dry in air.

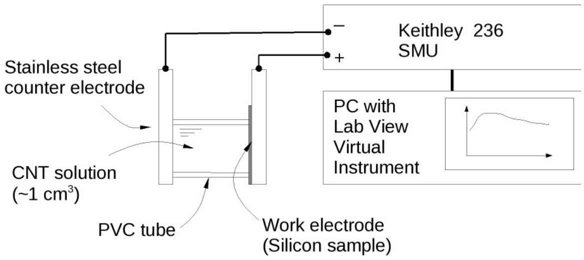


Figure 2: MWCNT Electrophorectic Deposition setup.

Electrical Characterization

The principle of FE is described by the Fowler-Nordheim model, in which the emission current density *J* is given by [2]:

$$J = \frac{c_1 \times \gamma \times E^2}{\phi} \times \exp\left(-\frac{c_2 \times \phi^{3/2}}{\gamma \times E} \right) \qquad (1)$$

where $J = I/A_{ef}$ (I: total emitted current, A_{ef}: effective emission area) c_1 and c_2 are constant, $E = V/d$ is the external (or macroscopic) applied electrical field (V: applied potential, d: electrodes separation distance), ϕ is the material work function and γ is called "field enhancement factor", that must be introduced in the equation when electrodes have protuberances [2].

From this model, it is expected that I-V curves obtained from FE devices show exponential-like behavior. Additionally, from V-d plot for a chosen emission current, it is possible to extract the macroscopic electrical field (*E*), which can be used as a quality parameter to compare distinct devices. Thus, samples with low *E* values have better emission characteristics because they need less energy to promote electron emission [3,7,8].

In order to measure the field emission current of electrons from the microtips, the devices (Si microtips samples) were mounted into a high vacuum chamber with pressure about 2 x10^{-6} Torr to avoid influences of residual gases ionization on the emitted current.

As illustrated in Figure 3, the Si sample is fixed on a cathode connected to ground through an electrometer (Programmable Electrometer model 617, Keithley Instruments), while a planar stainless steel anode, which has a circular area around 0.8 cm^2, is connected to the positive terminal of a high voltage source (High Voltage Supply model 248, Keithley Instruments).

A series protection resistor is included in order to protect instruments against current peaks due to undesired sparks into the chamber.

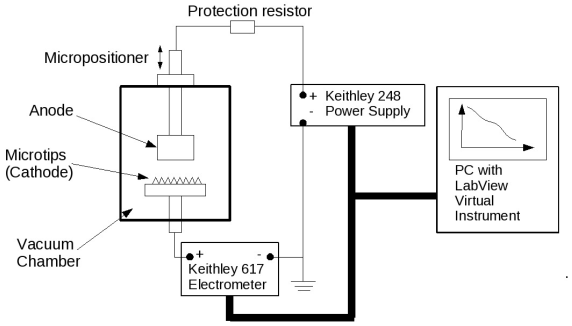


Figure 3: Electrical system setup for FE devices characterization.

A LabVIEW® Virtual Instrument software controls the high voltage source and stores the measured current values, showing graphically the results during the test.

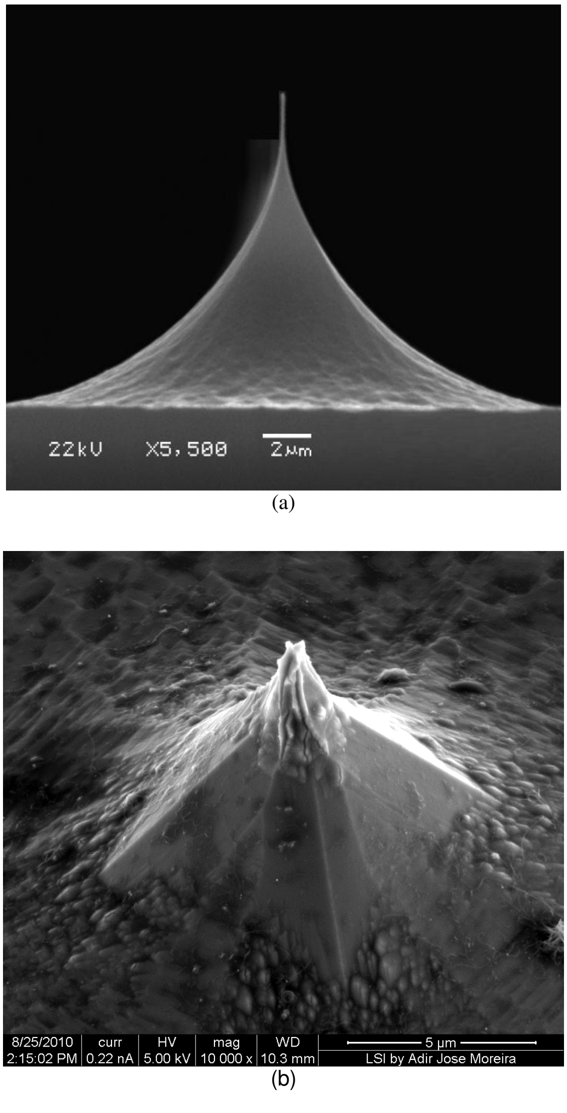
In this setup, the distance (d) between the sample and the anode can be adjusted externally by a micropositioner coupled to the anode, in such a way that electrical characterization can be made varying the electrodes distances, but keeping the vacuum environment conditions. Besides that, the anode structure has a self-aligned fixation system in order to compensate mechanical misalignment.

Electrical characterization was made by setting the electrodes distances from 60 to 170 µm for Si microtips sample without CNTs, and from 300 to 650 µm for Si microtips sample coated with MWCNTs. For each distance, a voltage ramp was applied limiting the maximum emission current about 20 µA in order to avoid eventual spikes and CNT burnout.

Results and Analysis

The morphology of the CNTs was observed by electron microscopy. A NOVA 400 NanoSEM (FEI Company™) scanning electron microscope (SEM) was used, operating at 5 keV to avoid damages on deposited CNTs.

Figure 4 presents images of the FE devices fabricated: (a) Si microtips without CNT and (b) MWCNTs electrophoretically deposited over silicon tips. In Figure 4b, one can verifies CNTs deposition over Si surface and it is pronounced on top of microtips, as expected, but such deposition looks like a CNT layer and no nanowire can be distinguished.



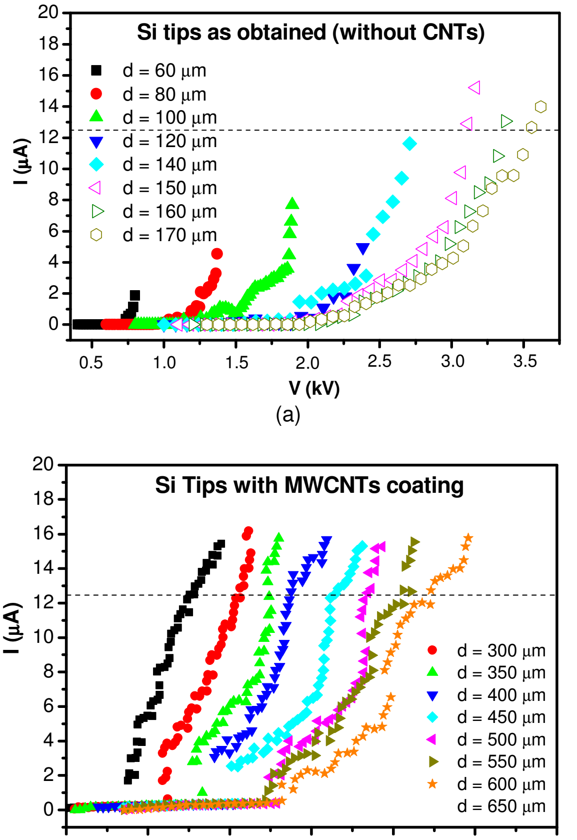
(a)

(b)

Figure 4: SEM images of silicon microtips: (a) Si microtip without CNT [7]*; (b) Detail of deposited carbon nanowires over one Si microtip.*

Results of electron emission characterization of Si microtips samples as obtained (without CNTs) and with MWCNTs coating are shown in Figure 5a and 5b respectively. I-V curves were measured for several separation distances (d) between electrodes. As expected, for a given current value, the raising of distance (d) follows an increase of the applied voltage required to obtain such current.

The reported tendency of exponential-like behaviour of both curves indicates agreement with FN theory [3]. One interesting aspect observed from these plots is that the applied voltage to obtain the same current level is quite different between the two samples (with and without CNTs): the device with CNTs shows electron emission from applied potentials below of 1 kV, for separation distances (d) higher than those applied on sample without CNTs. This behaviour could indicate the improvement of emission characteristics obtained from CNTs sample.



(a)

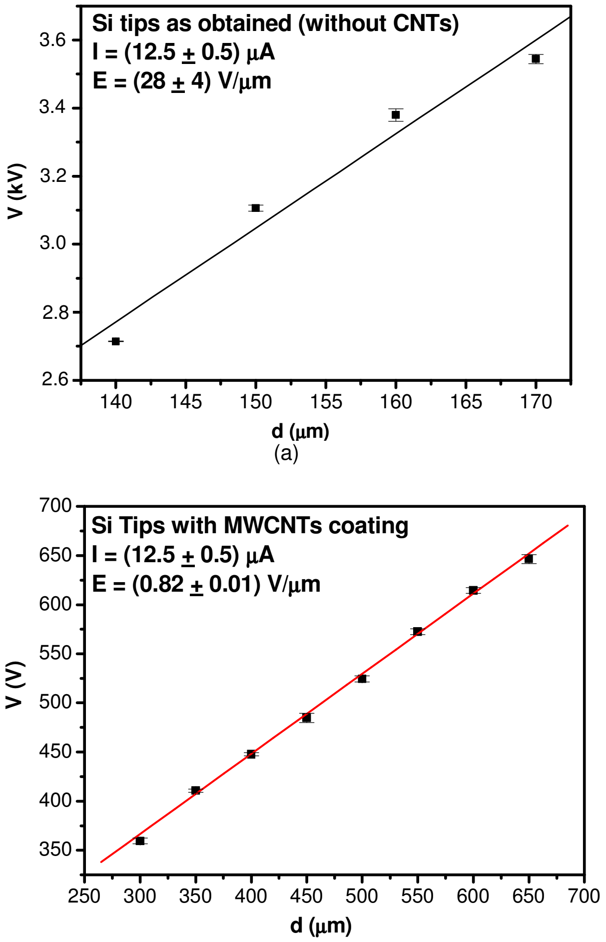
(b)

Figure 5: Measured field emission currents for samples (a) without CNTs and (b) with SWCNTs coating for several electrodes separation distances (d).

To quantify the efficiency of field emission, a given current value of 12.5 µA (dash lines from Figure 4) was chosen to compose a voltage versus distance (V-d) plot. From the slope of this curve, it is possible to extract the macroscopic electrical field (*E*), which avoids any mechanical systematic errors from (d) distance adjustments and also can be applied as a quality comparison parameter among distinct samples, as mentioned before. The V-d plots for Si device as obtained and with MWCNTs coating is showed for comparison in Figures 6a and 6b.

Both devices show a well-defined linear behavior of V-d plot, as expected. The slope of the fitted straight-line presents the macroscopic electrical field (*E*), which is around thirty five times lower for the Si + MWCNTs sample in comparison with Si sample as obtained. It is important to highlight that devices with better emission characteristics tend to show reduced *E*, or, in other words, they require less energy to promote electron emission. This indicates that the CNT deposition over Si tips was very effective in improving this device.

Note that even for higher separation distances (d) (650 µm – Figure 6b), the applied potential on the device with CNTs is clearly below the thousands of volts required to promote the same current level in the sample without CNTs for all separation distances d. These results indicate that in an integrated anode-cathode FE device (which separation distance (d) varies from some tens to units of µm), the required potential could be less than 100 V, which allows the development of compact sensor systems.



(a)

(b)

Figure 6: V-d plot for samples (a) without CNTs and (b) with MWCNTs coating.

Conclusions

In this work we have demonstrated that MWCNTs coating on Si microtips surface can improve the electron emission properties of FE devices, previously fabricated by HI-PS technique.

In the CNT deposition step, electrophoresis parameters as time and current/voltage, as well as the dispersion of CNTs in the solution, need to be more investigated to obtain homogeneous distribution of this material over the Si surface.

Although the samples did not show homogeneous coating of carbon nanotubes on the silicon surface and neither it has been possible to distinguish nanowires on the top of the tips through SEM, the electrical characterization indicated a significant reduction in the macroscopic electrical field necessary to extract the same level of emission current as obtained on Si devices without CNTs. Such result shows that MWCNT plays an important role in the electron emission process, and must be carefully investigated.

Thus, these preliminary results encourage us to continue the investigation of improved integrated FE devices for sensors applications.

Acknowledgements

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