Comparison between Single-Walled CNT, Multi-Walled CNT, and Carbon Nanotube-Fiber Pyrograf III

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Abstract: Single-Walled CNT (SWCNTs), Multi-walled Carbon Nanotubes (MWCNTs), and Carbon Nanotube-Fibers Pyrograf III PR-1 (CNTFs) were deposited by chemical vapor deposition under vacuum pressure value of (10^{-7} mbar). Their structures were investigated by field emission microscopy. Carbon Nano-Fibers Pyrograf III PR-1 showed an average fiber diameter within the range of 100-200 nm and a length of (30-100) µm. Single-walled Carbon Nanotubes were produced by high-pressure Carbon Monoxide process with an average diameter ranging between (1-4) nm and a length of (1-3) µm. Thin Multiwall Carbon Nanotube of carbon purity (90%) showed an average diameter tube (9.5 nm) with a high-aspect-ratio (>150). The research work reported here includes the field electron emission current-voltage (I-V) characteristics and presented as Fowler-Nordheim (FN) plots and the spatial emission current distributions (electron emission images) obtained and analyzed in terms of electron source features. For the three types of emitters, a single spot pattern for the electron spatial; distributions were observed, with emission current fluctuations in some voltage region.

1. Introduction

Multi-Walled Carbon Nanotubes (MWCNTs) and Single Wall Carbon Nanotubes (SWCNTs) [1-5] have a growing attention due to their perfect properties that make them the best candidate to be the next generation of field emitters such as, low turn-on fields, high emission current, stable emission current, long lifetime, low energy spreading, and high brightness [5,6]. In addition, Stacked-Cup Carbon Nanotubes (SCCNTs) or Carbon Nanotube-Fibers (CNTFs) have unique structures with highly graphitic as shown in figure 1. The graphene planes in the structures of (SCCNTs) or (CNTFs) have canted from the fiber axis, resulting in exposed edge plane on the interior and exterior surfaces of the fiber; CNTs, on the other hand, typically resemble an assembly of concentric cylinders of graphene [7-9].
Fowler-Nordheim (FN) first derived a semiclassical theory of FE based on physical assumptions and mathematical approaches; the theory has been modified many times over years to describe Cold Field Emission (CFE) from bulk metal where it is known as Fowler-Nordheim (FN) equation which is given by [10,11]:

\[ i = A_n \left( a \phi^{-1} (\beta V)^2 \right) \exp\left( -\frac{b \phi^3}{\beta V} \right) \]

Where \( i \) is the current emission, where it is exponentially dependent on the barrier width and, when graphically expressed on \( \ln(I/V^2) \) vs \( V^{-1} \) scales, will exhibit a linear relationship, \( \phi \) is the local work function, \( V \) is the applied voltage, \( a \) and \( b \) are the first and second FN constants, \( \beta \) is the local voltage-to-surface field conversion factor at some specific reference point on the emitter surface, and \( A_n \) is the national emission area defined by considering the local emission current density at the reference point. This equation uses the macroscopic field as an independent variable have often been used to describe CFE from Carbon Nanotubes (CNTs) including closed single-walled (CNTs) of small apex radius, particularly in technological context [12]. The Nanotube tip does not necessarily behave like a metal; electrons are not completely free and the effect of the tips atomic structure can be dominant. Moreover, an SWCNT is a three-dimensional structure (3D) and not an infinitely wide surface; thus, a more detailed treatment than the FN model is required. In this work there are three type of emitters: Single-Walled CNT, Multi-walled CNT, and Carbon Nanotube-Fiber Pyrograf III will be investigated and tested using a technique of the glass puller.
2. Experimental Details

Figures 2 and 3 showed the produced sample and the glass puller, respectively. Three types of CNTs were used: (a) Single-Walled Carbon Nanotubes (SWCNTs) were produced by high-pressure CO over Fe particles (HiPCO: High-Pressure Carbon Monoxide process), having an average diameter ranging between (1-4) nm with length (1-3) µm. (b) Multi-Walled Carbon Nanotubes (MWCNTs) Nanocyl™ NC7000 with 9.5nm diameter and high aspect ratio (>150), fabricated by chemical vapor deposition. (c) Carbon Nanotube-Fibers pyrograf III PR-1 (CNTFs), having average fiber diameter that is ranging between (100-200) nm, with the length of (30-100) µm.

Both tips prepared by employing a drawing technique using a glass puller apparatus (see figure 3), in this technique, two bearings are located accurately on plates supported by three stainless steel rods fixed rigidly to the frame of the control, this frame is strong enough to serve as a stable base for the instrument.

A glass tube (outside diameter=1 mm, internal diameter=0.1 mm) fits inside these bearings between the upper and lower chunks, with a furnace loop located around it. The CNTs were entered into the opposite end of each glass tube so they would protrude at the tip with wire plunger [13] the lower chunk spindle can slide vertically in order to pull down the glass tube under gravity, after preparing the emitters, they are mounted in a standard Field Emission Microscopy (FEM) with an emitter-screen distance of ~10 mm [14], and current limiting resistor of (100 MΩ) is used. The system was evacuated to pressure ~10⁻⁸ mbar after baking at ~170°C overnight. The FEM applied voltage V is increased slowly until a “switch-on voltage” V_sw is reached, at which point the emission current suddenly “switch-on”, at V_sw the current increase rapidly from about a Nano-
ampere to a much greater saturated value $I_{SW}$, by slowly decreasing the applied voltage to a lower value the emission current starts to be decreasing until limit reached, beyond which the emission current falls smoothly to zero as the applied voltage is decreased to the threshold value $V_{TH}$.

3. Results and Discussion

This section describes the results of experiments on the emission characteristics of the Carbon Nano-Fibers and Single-Walled Carbon Nanotubes. These results include the I-V characteristics, Fowler-Nordheim (FN) plot, and emission images. Emission current measurements are made using a pico-ammeter connected between the cathode and earth. As the applied electric field is slowly applied, the emission is only observed after a threshold field is reached, and emission suddenly jumps to a constant saturated value $I_{SAT}$, further increasing the applied electric field the $V_{MAX}$ will be reached, after that the tip explode, as the voltage slowly decreasing, the emission current fall to nearly zero, reaching the threshold value $V_{TH}$.

In the first set of specimens, we perform two sweeps of increasing voltage then decreasing voltage. Figure (4) showed the I-V characteristics for the three specimens, its related Fowler-Nordheim (FN) plot, and emission images (Fig. 4 (C), (D), and (E)) at $V_{SW}$. From the figure, it is shown that the $V_{SW}$ for SWCNTs, CNTFs, and MWCNTs are 800 V, 1100 V, 4300 V with emission current 4 $\mu$A, 1.2 $\mu$A, and 25 $\mu$A, respectively, the slope for SWCNTs, MWCNTs, and CNTFs is (-3294.54), (-6484.71), and (-1727.94) decayed V, respectively, and we notice that the MWCNTs gave higher emission current the SWCNTs and CNTFs, but the turn-on field emission at SWCNTs and CNTFs is lower than MWCNTs. The experiment is repeated for another sweep of increasing and decreasing the applied voltage, and the result shown in the figure (5).
From figure 5, it shows the same result as in figure 4, it seems from the figure and the experimental observation that the value of the V\textsubscript{SW} of the SWCNTs, MWCNTs, and CNTFs are 650 V, 1100 V, and 4500 V, respectively with emission current value 1.6 µA, 3.6 µA, and 23 µA, and there is
some emission current fluctuation in the low range in (MWCNTs-A4) emitter, due to their sensitivity to gaseous molecules [15]. As we decrease the applied voltage in the three specimens the saturated region extends down to $V_{\text{SAT}}$ value, which is for SWCNTs, CNTFs, and MWCNTs are 380 V, 750 V, and 1300 V with emission current 1.06 µA, 1.2 µA, and 1 µA. From the previous result, the emission current has been reduced by comparing the emission current between the first and second sweep of voltage, that would be referred to the existence adsorbate, and the variation of local electric field (F) [16]. The experiment has been performed on another set of specimens. Figure 6 shows the SWCNTs, CNTFs-26, and MWCNTs-A5 emitters.

The voltage and emission current range in the three emitters as following; in case of the SWCNTs the turn-on applied voltage value is $V=750$ V and the last applied voltage value in increasing voltage is $V=2850$ V, with emission current 2 pA, and 18.9 µA, respectively, CNTFs, the emission current turned on at applied voltage value 340 V to 1350 V, with emission current 30 pA, 8.49 µA, respectively, and MWCNTs voltage ranges from 1600 V to 2700 V, with emission current 8 pA to 6 nA. Figure 7 shows I-V characteristics and its relative FN plot.

The SWCNTs and CNTFs emitters’ shows switch-on phenomenon at $V_{\text{SW}}$ value = 1900 V, 1000 V, with emission current value 1.2 µA, 4.8 µA, respectively. As we continue increasing the applied voltage on SWCNTs specimen after switch-on phenomena appeared at $V_{\text{SW}}=1900$ V, $I_{\text{SW}}=1.2$ µA, the emission current suddenly raised from few µA range up to ~20 µA, that behavior appeared because the contribution of the adsorbate in the electron emission [17], as we decreased the applied voltage the saturation region extends down to $V_{\text{SAT}}$ value for SWCNTs, CNTFs, and MWCNTs are 1050 V, 1000 V, and 1750 V, with emission current value 3.99 µA, 1.11 µA, and 1 µA, respectively.
Figure 7(A) I-V Characteristics for SWCNTs and CNTFs (B) FN plot for SWCNTs & CNTFs (C) I-V characteristic for MWCNTs. (D) FN Plot for MWCNTs.

Figure 8. (A) I-V Characteristics for three type for specimen (B) Relate FN plot, where the slope value for SWCNTs, CNTFs, and MWCNTs are -16028.2, -1394.01, and -87187.2 respectively.

Figure 8 shows I-V characteristics and FN value during the decreased V. As we see from the figure 8, that the $V_{TH}$ for the CNTFs is less than SWCNTs, and MWCNTs and SWCNTs emitter gave
emission current higher than CNTFs, and MWCNTs. According to this equation:
\[
\gamma_{phe} = -6.44 \times 10^3 \phi^2 / K
\]
where \( \gamma_{phe} \) is the phenomenological field enhancement factor, and \( K \) is the slope of FN plot, the value of \( \gamma_{phe} \) for CNTFs will be higher than SWCNTs and MWCNTs, so that will explain the value of \( V_{TH} \) for the three type of the emitter[18, 19].

Figure 9 shows the emission image at \( V_{SW} \) for the second set of the emitter.

4. Conclusion
Three type of emitters have been tested, and all prepared with the same technique, by employing a drawing technique using a glass puller. Theoretically, the field emission from carbon nanotubes is a very challenging topic in many respects. Fundamentally, the field emission phenomena are highly non-equilibrium quantum mechanical processes that require the precise description of electronic structures of the nanotubes, and the equation of FN still in development to fully describe the electron emission from single-walled carbon nanotubes. From the result we can say that the SWCNTs and CNTFs have approximately similar behavior, while SWCNTs emission current turned on earlier, and that referring to the smaller radius of the nanotubes, but there are other influences on this matter, like the effect of the enhancement factor and field penetration, which the electric field can penetrate to CNTs to suppress the charge potential near the tip of tube and induce a few extra electrons [13], and the effective work function where its affected by the penetration of the electric field [18]. The cleanness the Carbon Nanotubes (CNT) surface effects on the current fluctuation, which is can be achieved by wet chemical cleaning and thermal post-treatment [19].
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