Use of tapered Pyrex capillary tubes to increase the mechanical stability of multiwall carbon nanotubes field emitters

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Abstract: In this study, Nanocyl™ NC 7000 Thin Multiwall Carbon Nanotubes (MWCNTs) were used with a high aspect ratio (>150) made by the process of catalytic chemical vapor deposition (CCVD). The field emitter tips were prepared by inserting these MWCT into fine glass capillary tubes that were pulled at high temperatures and then cut. Measurements were carried out under ultra-high vacuum (UHV) conditions with a base pressure of 10⁻⁹ mbar. The data show the effects of initial conditioning of MWCNT and hysteresis. Compression of the MWCNT by the capillary tubes appears to provide adequate mechanical support without requiring the use of a low-melting point electrically-conductive binder as has been used previously. Emission currents in excess of 1 μA were obtained so this technique shows promise as a reliable, stable, powerful electron source.

Keywords: Cold Field Emission, Carbon Nanotubes, Field electron microscope, Ultra High Vacuum, Fowler-Nordheim plot, Glass Microemitters.

1. Introduction

Efficient electron sources are the fundamental components of miniature vacuum tube sources for high frequency applications [1]. Many analytical instruments are used for elemental and mineralogical analyses [2]. Vacuum microelectronic devices that are radiation-insensitive and high-temperature tolerant for extreme environments electronic applications. Each application requires an electron source with specifically designed beam forming optics and emission densities that span a range of tens to hundreds of amperes per sq. cm. State-of-the art thermionic cathodes are ill-suited for miniature instruments because of their bulkiness, high temperature operation, and high power consumption. Conversely, state-of-the-art cold cathodes [3], based on atomically sharp micromachined tips [4, 5] are highly susceptible to poisoning when operated in non-UHV (10⁻⁸ to 10⁻⁹ mbar) environments.

A new class of field emitters was identified when carbon nanotubes (CNTs) were discovered [6]. Carbon Nanotube (CNT) based field emitters have been reported to exhibit high emission current with long-term stability, resulting from their high aspect ratio with small tip radius of curvature and high chemical inertness [7–9]. Thus a large amount of research is being carried out to utilize their excellent properties in practical applications, such as field emission displays (FED) [10, 11] and x-ray sources [12,13]. Another fascinating application of CNT emitters is a field emission backlight unit (FE-BLU) for liquid crystal displays (LCD) [14]. Although various types of lamps are being used as backlights for LCD, a cold cathode fluorescent lamp (CCFL) is by far the most widely used backlight for commercial LCD TVs and monitors [15].
Previous studies of field electron emission from and through glasses have had three aims. These include defining the mechanism for high-voltage breakdown [16, 17], creating stable bright electron sources, and studies of field emission from glass and metal-insulator composites [18]. Previous studies of field electron emission from glass with a conductive coating applied to the opposite side have been reported [19, 20]. In field electron emission electrons are emitted from the surface of a cathode under an intense applied electric field (> 3×10^9 V/m) [3]. The electrical current depends strongly on the work function of the emitter. In this paper, a new type of emitter is introduced that is based on Multiwall Carbon Nanotubes (MWCNTs) and fabrication techniques are presented with field emission data.

Previously glass and Pyrex capillary tubes have been used by our group to increase the mechanical stability MWCNTs as field emitters [20]. Then, the capillary tubes were filled with low melting point electrically-conductive materials such as indium, tin, and gallium, and heated the tubes to a temperature just below the melting point so that the tube softened and then necked at several points along its length. After each tube was slowly cooled to room temperature it was cut at these constrictions to form several field emitters, each having an apex at the point where the tube was cut.

2. Experimental

We used apparatus similar to what was used before, as shown in Fig. 1, to prepare agglomerates of MWCNT in tapered PyrexTM tubes having an inside diameter of 0.1 mm and outside diameter of 1.0 mm to provide physical support for the MWCNT [20]. A Nichrome wire was used to heat a single straight tube as shown in Fig. 1.b, to taper the tube to much smaller inner diameters at several locations as shown in Fig. 1.c. Then the tube was cut to form several tapered sections that were filled with MWCNT to form the field emitters. NanocylTM NC 7000 Thin Multiwall Carbon Nanotubes (Nancyl S.A., Sambreville, Belgium) were used, which have a typical diameter of 9.5 nm and aspect ratio greater than 150. After each tube was filled with the MWCNT a tungsten wire having a diameter of 0.1 mm was inserted into the end which was not tapered to make a permanent electrical contact with the MWCNT.

Prepared emitters were investigated in a locally built point to-plane field electron microscope (FEM), with an axial tip to-screen distance of 10 mm [21]. The FEM was evacuated to ultra-high vacuum conditions by the combination of a rotary pump (which produces a backing pressure of about 10^-3 mbar) and an oil diffusion pump system, connected to a liquid nitrogen (LN2) trap. Without baking, the FEM reaches a base-pressure of about 10^-7 mbar. The pressure reaches about 10^-9 mbar after baking the system for 12 hours at 180°C, and adding liquid nitrogen to the trap [22]. In operation, the FEM applied voltage V is increased slowly until a "switch-on voltage" V_{SW} is reached, at which point the emission current suddenly "switches on". At V_{SW} the current increases rapidly from about a nano Ampere to a much greater saturated value I_{SAT}, similar to the phenomena that has been previously reported [23-24]. The current-voltage (I-V) data yields a FN plot that has linear segments.
FIG. 1. (a) Apparatus used to prepare the Pyrex tubes that were used to hold the MWCNT; (b) Nichrome wire heater used to heat the tube to taper it to a smaller diameter; (c) Pyrex tube tapered at several locations where it is cut to form the field emitter tips.

Figure 2 is an SEM image of one of these field emitters in which the tapered end has an opening with a diameter of approximately 184 nm. An agglomerate of MWCNT is held securely by pressure at the opening without requiring the use of epoxy, pitch, or other agents for attachment. An EDX (energy dispersive X-ray spectroscopy) analyzer was used to determine the composition of the emitter surface which was primarily carbon, oxygen and sodium.

FIG. 2. SEM image of the completed field emitter for which the tapered end has an opening diameter of 184 nm.

3. Results and Discussion
The field emitter shown in Fig. 2 was placed in a vacuum chamber in which a phosphor screen at a distance of 10 mm was used as the anode. The chamber was evacuated to a base pressure of $10^{-9}$ mbar. Current vs. voltage measurements were manually recorded using a Keithley 485 Picoammeter and a high-voltage power supply with a digital voltage readout. The potential was increased in steps of 100 V. Figure 3 is a Fowler-Nordheim (F-N) plot for these measurements made with the field emitter that is shown in Fig. 2. The plots in the figure represent the I-V measurements which were repeated as the voltage was increased or decreased in steps.

![Fowler-Nordheim plot](image)

**FIG. 3.** Fowler-Nordheim plot of current vs. voltage measurements made with the field emitter shown in Fig. 2. The data are plotted for the first and second time that the voltage is increased and decreased.

Figure 3 shows the effects of conditioning of the emitter as well as the hysteresis. Note that as the voltage is increased ($1/V$ decreased) for the first time (1-Up), the initial value of the current, normalized by dividing by the square of the voltage ($I/V^2$), is greater than its value at same point during later cycles. This effect is referred to as the “initial conditioning” of the MWCNT. Also, as the voltage is lowered in the reverse cycle of the hysteresis loop (1-down), the normalized current is greater than in the former part of the hysteresis loop. Subsequent loops are similar to 2-up and 2-down in the second loop.

In conclusion, using compression by a Pyrex capillary tube to mechanically stabilize the MWCNT made it possible to avoid adding pitch, Epoxy, or other materials that would increase the electrical resistance and thermal resistance required to lower the maximum current, and may also contaminate the emitter. We have already obtained currents in excess of 1 μA (Fig. 3) without requiring such binders.

4. **Conclusion**

In summary, using compression by a Pyrex capillary tube to mechanically stabilize the MWCNT has made it possible to avoid adding pitch, epoxy resin, or other materials. Such materials might increase the electrical resistance (and hence lower the maximum current), or increase thermal resistance (and hence potentially make the emitter less stable), or contaminate the emitter. Currents in excess of 1 μA (Fig. 3) without requiring such binders, were obtained.
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