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DIRECT GROWTH OF MULTI-WALLED CARBON NANOTUBES ON SHARP TIPS FOR ELECTRON MICROSCOPY

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The favorable electron optical properties of carbon nanotubes (CNTs) have been studied in detail, but the application to electron sources has been limited by the complexity of the fabrication process. We report the use of Plasma Enhanced Chemical Vapor Deposition (PECVD) for the direct deposition of multi-walled CNTs onto the apex of sharply etched tungsten tips, aligned to the vertical axis of the tips. We show that these emitters have excellent stability.

Keywords: Carbon nanotubes; electron microscopy sources.

1. Introduction

Carbon nanotubes (CNTs) have been of particular interest to research since their discovery by Iijima[1] in 1991. Synthesis methods include the arc discharge method[2] and laser ablation,[3] which produce long, low-defect CNTs of varying diameter and length commonly contained within amorphous carbon. However, the plasma-enhanced chemical vapor deposition (PECVD) method, first discovered six years later,[4] allows for the accurate positioning of CNTs wherever desired[5] and for the control of length, diameter and alignment.[6]

Whenever the structure of the CNT is not critical, the PECVD method is ideal and has already been applied to field-emission displays,[7] microwave amplifiers[8] and transistors.[9] But PECVD-produced CNTs, which form at $\sim 650°C$, tend to have more imperfections[10] than those produced by the arc discharge method[11] which typically form at $\sim 2000°C$. Consequently, CNTs produced by PECVD have not, as yet, been applied to devices where a highly graphitic, crystalline structure is required, such as for electron sources in electron beam equipment.

To test field emission from graphitic CNTs, processes have been developed to remove the amorphous carbon surrounding CNTs produced by the arc discharge method.[12] CNTs are then manipulated utilizing microprocessing techniques and attached to an etched tungsten tip (which has a high field enhancement) to determine field emission characteristics. Though the emission characteristics of the CNT have been found to be very promising,[13] the attachment process is extremely

cumbersome; the length the CNT protrudes from the tip cannot be controlled, neither can the CNT's alignment, nor can it be certain what the contact between the nanotube and tungsten wire is. Electron source manufactures are unlikely to invest in CNT electron sources until a simplification of the process to position high-quality nanotubes onto tungsten tips is developed and proven to work so that the production of such tips can be scaled up to mass production.

We propose that PECVD is the solution, as most of this process can be automated and the process is scalable (i.e., it is possible to grow many tips simultaneously). We describe three significant challenges that have been overcome. Riley *et al.*[14] have already shown that a forest of highly defective CNTs can be grown on a tungsten tip by thermal chemical vapor deposition (TCVD), but in order for electron beam equipment to work effectively, there must be only a single source of electrons, hence a single CNT. As CNTs grow from a catalyst particle, the first challenge is to place a single catalyst particle at the vertex of the tip by the simplest and most reproducible process possible. The second challenge is to ensure that the nanotube is aligned in-axis with the rest of the tungsten tip. The third challenge is to improve the quality of the nanotube formed at the top of the tip. This can be achieved by employing a new technique first reported by Minoux *et al.*[15] where the CNTs are thermally annealed following deposition.

2. Experimental Method

Tungsten tips 125 μm in diameter and approximately 10 mm long were etched to an apex radius of 200 nm for proof of concept, and to a radius of between 20 and 30 nm at Philips Research Laboratories (PRL), Eindhoven, The Netherlands. The tips were then placed in a sputter-coater, with their axes aligned perpendicularly to the plane of the sputter target. 15-nm ITO was deposited. ITO is required to act as a diffusion barrier, as metal catalyst deposited on a bare tungsten wire will diffuse into the tungsten itself when molten, thus preventing the formation of catalyst particles to nucleate CNT growth. Subsequently the tips were then either placed into an evaporator, or kept in the sputter coater, and a 5-nm layer of Ni deposited. The tungsten wires were then cut to a length of ~ 8 mm and placed in a fully automated Black Magic PECVD reaction chamber (Nanoinstruments Ltd.) for CNT growth.

The tips were ramped to 750°C at 300°C/min and NH_3 inlet at 120 sccm, raising the pressure to 3.4 mbar. Upon reaching 750°C, C_2H_2 was inlet at 30 sccm raising the total pressure to 4.5 mbar. A potential of 640 V was applied between the gas showerhead and the tip to initiate the plasma. The growth was performed for 15 min, producing CNTs of radius 20 nm and height 500 nm.

3. Results

Uniform and repeatable growth can only be achieved when the growth conditions are tightly controlled and stable. Tips 200 nm in radius at the apex exhibited repeatable uniform growth (as shown in Fig. 1). Note that the process used produces tips on which the CNTs are all aligned to the vertical axis of the tip.[16]

The growth of CNTs on W wire only 20–30 nm in radius at the apex proved more difficult to control when the catalyst was deposited by evaporation. Evaporated Ni tended to agglomerate at the apex often resulting in the tip having a globular, wavy structure at the end (see Fig. 2).

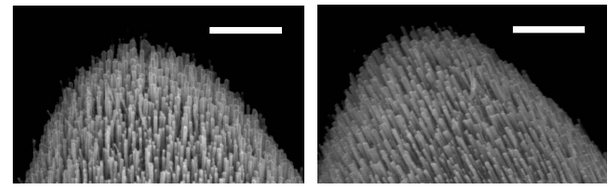
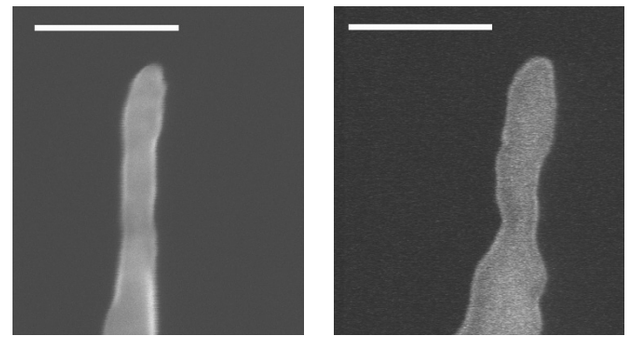


Fig. 1. Uniform growth of CNTs on two etched W tips of radius 200 nm. Note all CNTs are aligned axially. The scale bar is 500 nm. The Ni catalyst was deposited by sputter coating.



(a) (b)

Fig. 2. W tip (a) before and (b) after Ni evaporation. ITO has already been deposited. The scale bar is 200 nm. The tip has clearly grown but in a nonuniform way, with more catalyst forming in some areas than others. Such deposition will not produce repeatable results.

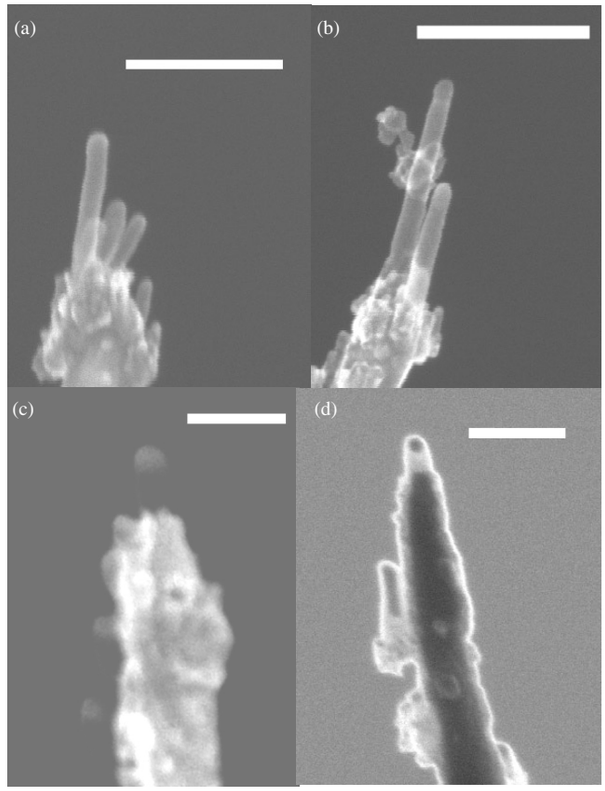
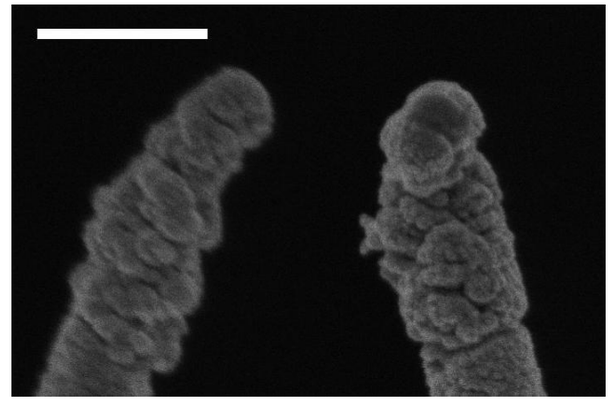


Fig. 3. (a) and (d) show multiple CNTs grown at the apex of sharp W tips, (c) and (d) show single CNTs grown at the apex of sharp W tips. The scale bar is 200 nm. Ni catalyst particles can clearly be seen in the bottom images. The Ni catalyst was deposited by evaporation.



(a) (b)

Fig. 4. W tip (a) before and (b) after Ni sputter coating. ITO has already been deposited. The scale bar is 200 nm. The tip has clearly grown but in a more uniform manner than by evaporation. This method is much more promising for catalyst deposition.

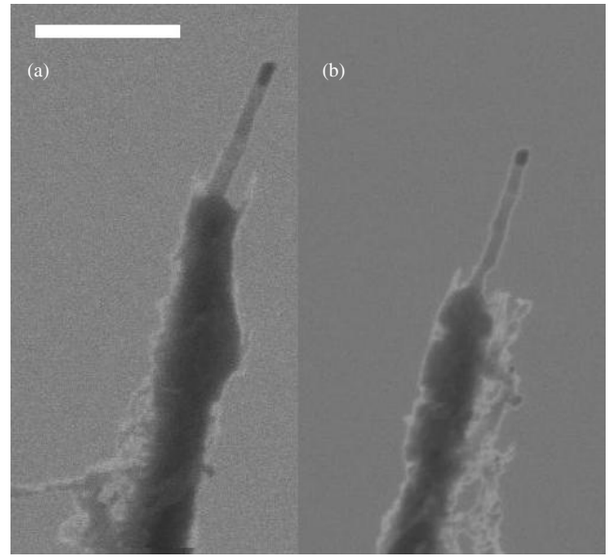


Fig. 5. (a) and (b) show single CNTs grown at the apex of sharp W tips. The scale bar is 200 nm. Ni catalyst particles can clearly be seen at the top of the CNTs. The Ni catalyst was deposited by sputter coating. Note that the CNTs are aligned with the axis of the tip.

Despite catalyst difficulties, the catalyst deposited was still enough for CNTs to nucleate and grow at the apex of the tip, though the advantage of the apex's small dimensions was somewhat diminished by the relatively large amount of catalyst. The consequence was a number of multi-source tips, i.e., tips where more than one CNT has grown at the apex (as shown in Fig. 3).

For single CNTs grown at the apex, the diameter is controlled by the radius of the apex. Indeed, the CNT diameter is approximately equal to the radius of the apex.

Ni catalyst deposited by sputter coating, unsurprisingly, provides much more reliable results (as seen in Fig. 4). Films deposited by sputter coating tend to produce more repeatable results due to the slower deposition rate and they give a more uniform coating around the tip than evaporation, where the exact angle at which the tip is mounted will be more critical to the uniformity of the coating (Fig. 5). Due to the geometry of the tip, much more catalyst is deposited at the apex of the tip compared to the sides. Consequently, if the amount deposited is tightly controlled, CNTs will only grow at the apex, and much further down the shaft of the tip. Therefore, the CNTs at the tip are isolated from the others at the base and will see a much higher field with resultant field emission only coming from those CNTs at the tip.

4. Field Emission Characteristics

The variation of current with field from a field emitter is dictated by the Fowler–Nordheim (FN) theory of field emission,[17] and has been applied to CNTs on tips elsewhere[18] which have been shown to exhibit typical FN behavior. The key determinant as to whether CNTs can be seriously considered as an electron source in its stability over both short and long periods of time. Experiments by de Jonge *et al.*[18] have shown that CNTs attached by a "cut-and-stick" method exhibit strong stability over both long and short periods of time when running at a temperature of 500°C. Running the tip at this temperature drives the adsorbates off the CNT during field emission. It has not been shown thus far whether CNTs deposited directly show this same stability.

Figure 6 shows the short-term stability of the CNT in Fig. 3(d). It shows the CNT current varying by only 0.5% peak-to-peak which is slightly more than de Jonge's CNTs attached by a cut-and-stick method. However, this CNT was run at room temperature, so exhibits promising stability.

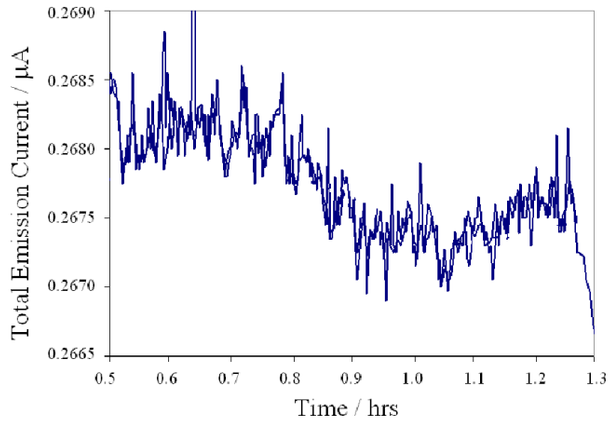


Fig. 6. Total emission current stability over 50 min for the CNT shown in Fig. 3(d). The peak-to-peak variation is 0.5%.

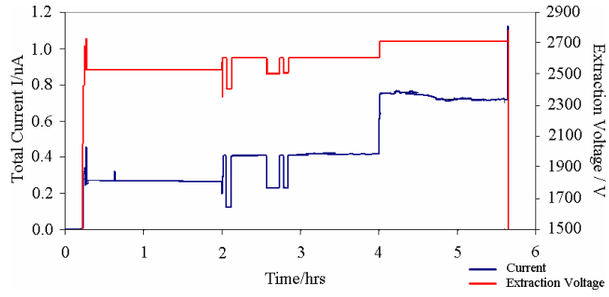


Fig. 7. The stability of total current at various extraction voltages. The CNT shows good response to variations in extraction voltage suggesting it is a robust possibility for field emission sources.

The CNT also has a good response to the applied extraction voltage. Figure 7 shows the CNT's response to four voltages. It exhibits repeatable field emission currents at various voltages and shows good stability up to the highest extraction voltage applied.

5. Discussion

Cold field emission sources in use today, such as tungsten, have the highest brightness and lowest energy spread of electron sources available (see Table 1).

However, cold field W sources are limited by poor stability. One of the main factors, electromigration of W atoms at the apex of the source, is a consequence of the high fields used to extract electrons from the W tip. Another factor is ion bombardment. Ions formed from bombardment by electrons are attracted to the negatively biased electron sources and attach to the tip thus changing the workfunction.[19] These factors combined contribute to the current varying by as much as 5%.[20]

CNTs overcome this problem because their sp^2 covalently bonded structures are much stronger than W metallic bonds, so atoms are not as likely to rearrange at the apex when a high field is applied which results in the excellent stability observed.

Previous work on CNT electron sources was carried out on CNTs manually attached to tips by employing micromanipulation techniques. Closed-cap CNTs were observed to exhibit the best stability and emission pattern[21] with a reduced brightness measured to be over 10^9 $Am^{-2}sr^{-1}V^{-1}$ (an order of magnitude higher than commercially available electron sources) and energy spread of

Table 1. Table comparing the brightness and energy spreads of commonly available electron sources (courtesy of FEI Company, Oregon, US).

Electron source	Brightness (A/cm^2sr)	Energy spread (eV)
Schottky	5×10^8	0.3–1.0
Cold Field W	10^9	0.2–0.3
LaB_6	10^7	1.0
W	10^6	1.0

0.1–0.6 eV,[18] which is as good as the tungsten cold field emitter.

The breakthrough here is the direct growth of CNTs aligned to the vertical axis of a tungsten tip by PECVD. The tip is millimeters long, but this technique allows for the accurate positioning of single CNTs without the use of lithography for use as electron sources.

6. Conclusion

CNTs may offer low-extraction voltage, high brightness solutions to electron microscopy demands. The challenge has been to develop a process to enable bringing CNT electron source devices to market. This fabrication method, scalable to mass production, allows for the first time the direct deposition of aligned CNTs onto tungsten tips.

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