The application of carbon nanotube electron sources to the electron microscope.

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ABSTRACT

The promising field emission properties of carbon nanotubes, or CNTs, have resulted in them being identified as desirable sources for electron microscopes and other electron beam equipment. A new process to grow single CNTs aligned to the electron-optical axis inside electron source modules has been developed. The process involves putting the entire source-suppressor module inside a plasma-enhanced chemical vapour deposition reaction chamber. This is a process which can be scaled up to mass production. The resultant CNT electron sources were inserted into an electron microscope for imaging. Though current stability was found to be comparable to the tungsten cold-field emitter (with a maximum-minimum variation of 3-7% of the mean current over one hour), the reduced brightness was found to be an order of magnitude greater than a typical Schottky source (at 3×10^9 Acm^2sr^{-1}) with a kinetic energy spread of 0.28 eV. Imaging with a CNT source has produced a marked improvement in resolution when compared to a Schottky source using the same electron-optics. The properties measured show that the CNT source compares favourably with and in some cases improves upon other sources available today. In particular, the CNT source would be of most benefit to low-voltage, high-resolution microscopy.

Keywords: Electron microscope, electron source, carbon nanotube, CNT, electron gun, tungsten tip.

1. INTRODUCTION

Since carbon nanotubes (CNTs) came to prominence following the Iijima paper[1] of 1991, there has been extensive research into their properties, synthesis and possible applications. In particular, much research has focused on the use of CNTs for field emission sources because they have several advantages over other field-emitting materials including high aspect ratio (hence a high field enhancement and brightness), a high Young's modulus, strong covalent bonding preventing electromigration of surface atoms and a high conductance[2]. With these favourable properties, CNTs are particularly advantageous for electron sources for electron microscopy. Research by De Jonge et. al.[3] has found CNTs to have high stability, a kinetic energy spread as little as 0.2 eV and reduced brightnesses of the order of 10^9 A/srm^2V, significantly better than state-of-the-art sources available today.

To test field emission from graphitic CNTs, processes have been developed to remove the amorphous carbon surrounding CNTs produced by the arc discharge method[4]. 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 promising[5], the attachment process is extremely time-consuming; 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. It certainly isn't a method that can be scaled up to mass production of CNT tips.

Direct growth of CNTs onto tungsten tips by plasma-enhanced chemical vapour deposition (PECVD) offers a straightforward approach to solving these problems. Work reported elsewhere has demonstrated the principle of growing aligned, single CNTs onto tungsten tips with a specially designed stage and by limiting the number of CNTs grown at the tip by controlling the radius of the tungsten tip[6]. It also negates the need for lithography, which is technically complicated and offers no real advantage over attaching CNTs to tungsten tips.

However, whilst the method was successful in growing single CNTs onto tungsten tips, the yield of single tips was not equivalent to industrial yields of other electron sources (typically 70%) with little control over the dimensions of the grown CNTs – it should be noted that there hasn't been any work in the literature that determines just how important it is to have a single CNT grown on a tungsten tip. It was also found difficult to align tungsten tips in testing chambers once grown due in part to their increased brittleness, with kinetic energy spread measurements being particularly difficult to obtain. An alternative approach has been to grow a CNT directly onto a pre-aligned etched polycrystalline tungsten wire already mounted in an electron source module. This paper further outlines the improved growth of single CNTs with such a setup, post-treatment processes developed, details of the resultant field emission and early-stage electron micrographs with CNTs as the electron source.

2. EXPERIMENT

It is important that beams in electron microscopes originate from one CNT. If they do not, the beams from the individual CNTs will interfere and they will also have different energies because the local field will be different. Consequently, growth must be optimized so that most tips result in one CNT grows at the top.

Mounted polycrystalline tungsten tips were etched to a radius of 100 nm and mounted in an electron source module as shown in figure 1, protruding from a centrally located hole in a suppressor, by 50-100 µm. The modules were then transferred to a sputter coater and coated with a 15 nm thin film of ITO followed by 8 nm Ni.

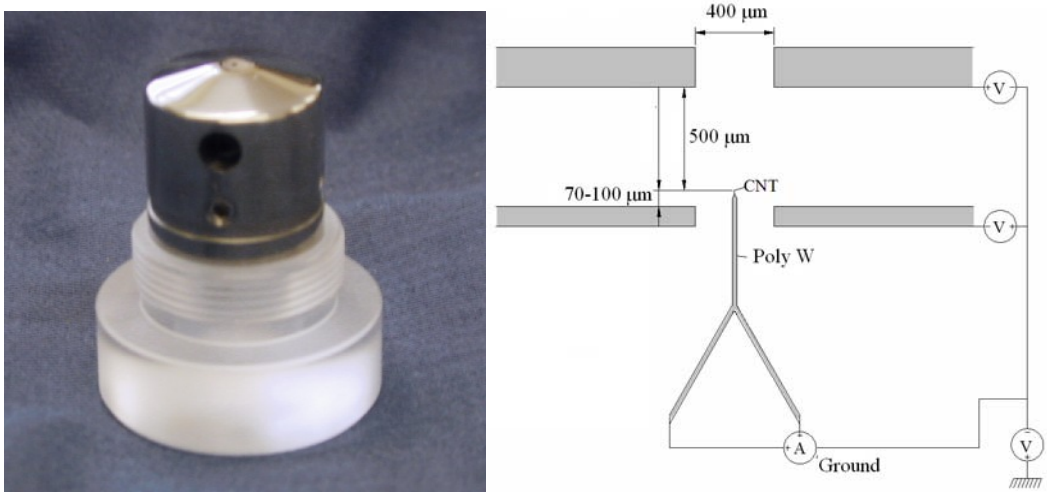

Figure 1: Left, a picture of typical electron suppressor module. Right, a schematic diagram of the set-up used to extract current from the CNT. The piece of metal through which the CNT-W structure protrudes is the suppressor.

Subsequently, the entire electron source module was placed into an AIXTRON Black Magic plasma-enhanced chemical vapour deposition system incorporating a specially designed stage consisting of a graphite heater and supporting ceramic. A metal contact shorted the suppressor to the tip and the module was positioned so that the apex of the etched tungsten tip was at the height of the stage, being in both physical and electrical contact with the heater. The setup was similar to that described by Mann et al[6]. The system was pumped down to a pressure of 0.2 mBar. Ammonia was then leaked into the system at a rate of 200 sccm raising the pressure to 2 mBar. Simultaneously, the graphite heater was

heated resistively to 750 ºC at a rate of 300 ºC/min. Upon reaching 750 ºC, the heater was held at this temperature for four minutes to allow the entire module to reach this temperature. Plasma was ignited with a potential of 640 V dropped between the showerhead positioned 4 cm above the graphite heater and the stage. This was swiftly followed by leaking in 50 sccm of acetylene, raising the pressure to 2.5 mBar. The temperature of the heater was measured by a thermocouple with a set-point of 750 ºC being maintained throughout the 30 minutes of growth. After the process was completed, heat, plasma and gas flow were terminated simultaneously and the electron source module allowed to cool.

3. RESULTS

Given that the whole electron source module was placed in the sputter coater for catalyst deposition, the resultant growth of CNTs covers not only the tungsten tip but also the top surface of the suppressor. The suppressor-tip module is standardized so that any part can be replaced. For growth, a dummy suppressor is used so that after growth this can be replaced with a clean one for field emission measurements.

Of the electron sources made most recently by this method, single CNT tips with a success rate of approximately 75% were produced. Four such CNTs are shown in figure 4. The dimensions of the CNTs grown were similar to previous processes, with heights varying from 400-500 nm.

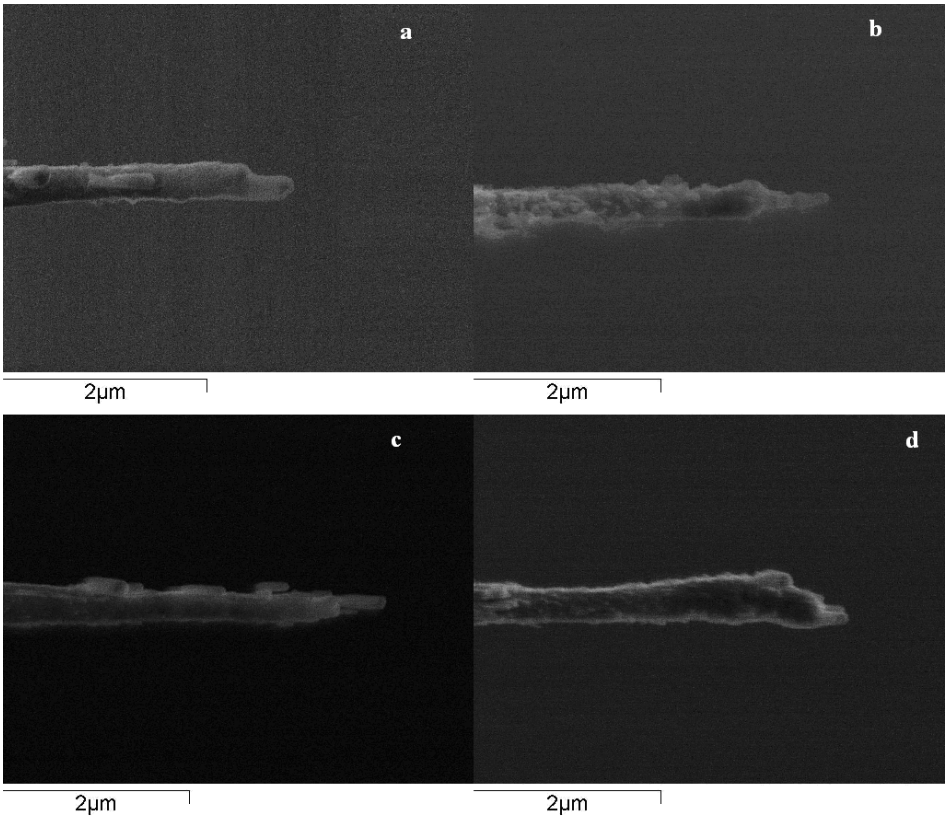

Figure 2: Three single CNTs grown on tungsten tips and a double tip mounted in electron sources. The tips have the following approximate dimensions: (a) length 450 nm, diameter 170 nm (b) length 450 nm, diameter 80 nm (c) length 460 nm, diameter, 80 nm (d) length 240 nm, diameter 70 nm. Note (d) is a double tip with the secondary CNT likely to adversely affect field emission.

CNTs grown by PECVD contain many more deformities than those grown by arc discharge or laser ablation. This is because the CNTs grown by the latter methods are produced at much higher temperatures than PECVD, thus creating a more crystalline structure. Arc discharge and laser ablation CNTs come with the disadvantage that there is no way of controlling the rate or the direction in which the CNTs will grow. The most crucial point for CNTs, however, is their tip structure, since that is where the electrons will be emitted from. When the PECVD process stops, the Ni is coated in an

amorphous carbon layer. This is because the process is being halted effectively half way through. A process has been developed to complete the crystal structure at the top of the CNT and this improves the quality of the electron beam when it has been carried out.

Minoux et al.[7] reported that CNTs crystallize when subjected to high temperatures at low pressure (~10^{-6} mBar). This process of annealing to improve the graphitization of CNTs was shown to happen on silicon substrates, but this does not necessarily translate to CNTs grown on tungsten. Experiments to determine whether this process can be successfully applied to carbon nanotubes on tungsten tips were carried out. Tests have indeed shown that there is a distinct improvement in the crystallinity of CNTs subjected to 1400 K for 6 mins at an initial pressure of 3×10^{-6} mBar as shown in figure 5.

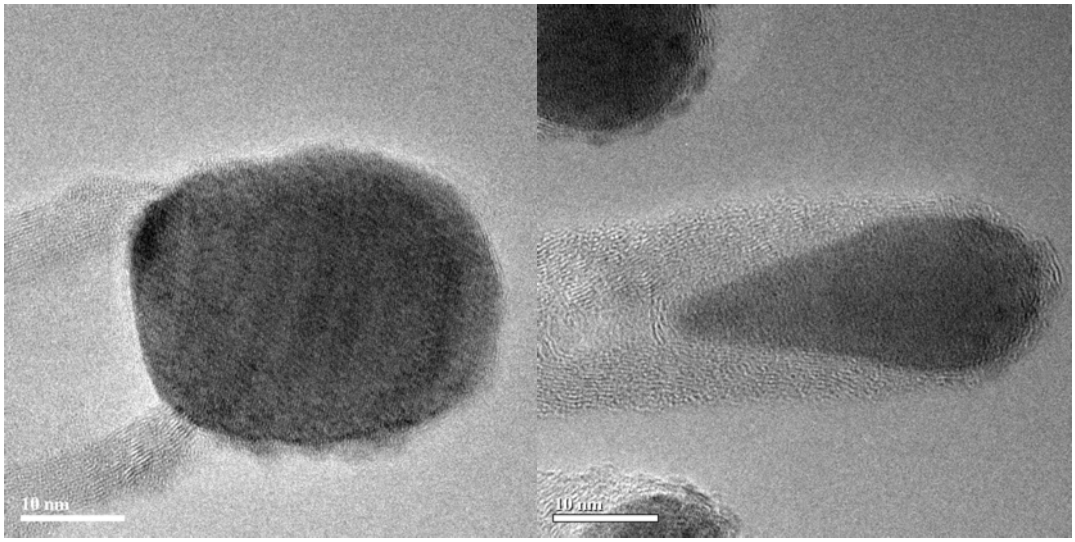

Figure 3: Left, TEM micrograph of the cap of a typical CNT grown from Ni catalyst at 750 °C. Note the disordered and amorphous cap structure without the wall-like graphene structure observed further down. Right, shows a CNT that has been annealed for 6 mins at 1400 K and 3×10^{-6} mBar. Graphene structure is clearly visible all the way around the cap; there is clearly a marked improvement in the CNT as a consequence of the annealing process. Both scale bars are 10 nm.

Therefore, following growth of the CNT on the etched tungsten emitter, the latter was heated in a Field Electron Emission (FEM) system, firstly in order to complete the end-cap on the CNT and hence get emission on the optical axis of the emitter and secondly to remove adsorbates which cause instability. Figure 1 shows a schematic diagram of the experimental set-up used in the FEM. The emitter was heated in-situ for periods ranging between 8-10 hrs at elevated temperatures (>1000 K) until the emission stability reduced to within ~5-10% of the mean for extended periods exceeding 1 hr. The emission stability obtained from the CNT cathodes are of levels similar to those obtained from conventional cold field emitters used in electron microscopy[8]. However, this value is still too high and current work is focussed on chemically removing species adsorbed onto the entire Schottky base as a result of the growth process.

One such CNT cathode is shown in figure 6 with its corresponding field emission pattern. The pattern indicates field emission from the CNT with a characteristic, circular emission pattern. Were the emission to come from tungsten, the crystal planes of the tungsten would be observed instead and the extraction voltage would exceed 3 kV. The emitter also required flashing at a temperature of ~1200 K for several minutes to restore emission stability, in a similar manner to cold field emitters currently used in SEMs.

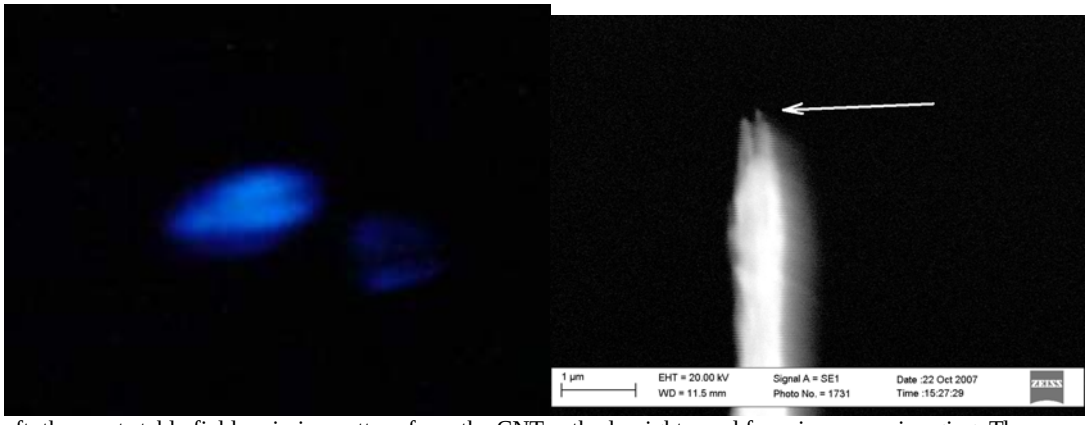

Figure 4: Left, the most stable field emission pattern from the CNT cathode, right, used for microscopy imaging. There appear to be at least five CNTs at the apex. The topmost CNT, indicated by the white arrow, extends significantly higher than the rest. Blurring is due to charging.

Following characterization of the CNT, the source was transferred to a single lens electrostatic electron column. This work was carried out at York Probe Sources Ltd. The lens system consisted of three parts, the extractor, a lens electrode and a ground electrode. Because this rig was designed to only test the alignment of electrostatic electron columns with Schottky emitters, only a comparison between Schottky emitters and CNT emitters can be made with the same testing rig geometry. An improvement should still be visible, however.

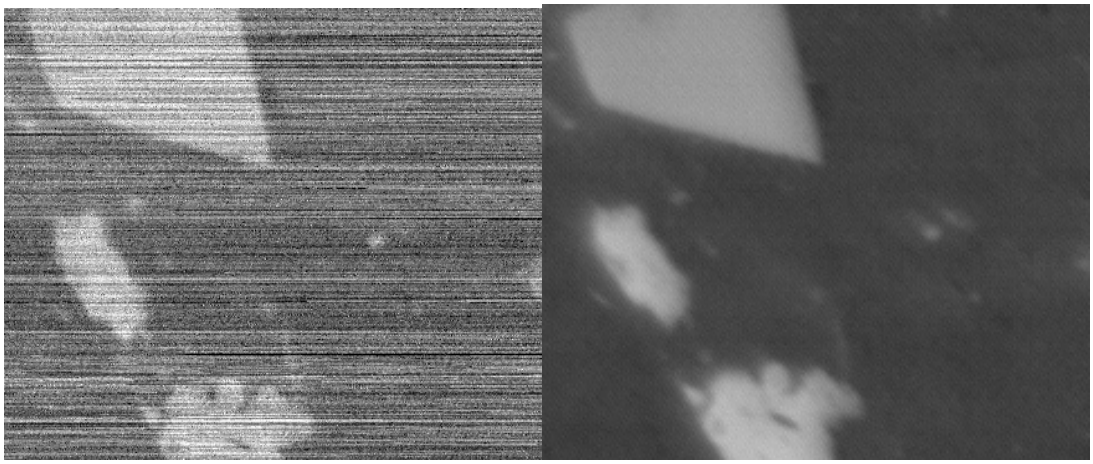
Figure 5: Left, a scanning electron micrograph using a CNT source which can be used to compare the resolution and stability of a typical SFE micrograph shown right. Whilst the CNT image is much noisier, the objects in the image are sharper. Pay particular attention to the improved resolution in the edges of the object with straight sides at the top left of the image. It is otherwise very difficult to see a difference.

When the CNT ensemble was placed in the microscope, the operational parameters, as expected, were different from that of a Schottky emitter. A total emission current of 2-5 µA was used. The extractor voltage was 1000 V and this resulted in a specimen current of 10 nA. Figure 5 compares the same artefacts on a TEM grid imaged with a Schottky emitter and a CNT emitter. Horizontal banding can be seen in the image, which is in part due to the acquisition software with low sample currents and also an indication of the inherent instability of the CNT emitter, but the artefacts in the image with the CNT emitter are more clearly resolved.

It is difficult to see in figure 7 that there is greater resolution with the CNT source. More work with a mores stable CNT is required to confirm improved resolution. However, given that the beam current used for the CNT source was an order of magnitude less than that of the Schottky (150 µA), that the beam kinetic energy used was 5 keV (rather than the 7.5

keV used for the Schottky) and that the beam defining aperture subtended an angle of 27 mrad (rather than the 8 mrad used for the Schottky), by geometrical arguments, the reduced brightness of the CNT source is a factor of 10 times the brightness of the Schottky emitter. This means that the CNT brightness is of the order of 3×10^9 $Acm^{-2}sr^{-1}$, which would be a significant improvement even on tungsten field emission sources. By similar arguments, the energy spread of the beam was determined to be approximately 0.3 eV.

4. DISCUSSION

For CNTs to become a feasible electron source, there needs to be a reproducibility in manufacture. Manufacturers of electron microscopes desire a source that will produce similar field emission properties for each tip. This cannot happen if every tip is different. This process improves upon previous work because it replicates system parameters more precisely from tip to tip. It is also easier to align the CNT with the axis because of increased control over the suppressor's orientation. It also shows that there isn't a need to position CNT growth by lithographical means since secondary CNTs are unlikely to affect field emission.

With the modules already aligned for use in electron columns, this is a self-aligning process with the CNTs growing on axis and along it vertically from every tip which gives the best chance of extracting high quality electron beams from the CNT. This is potentially a very powerful process and it would be straightforward to integrate into existing electron source manufacturing technology and thus bring CNT electron sources to market in the very near future. Improvements must be made to stability however and is the focus of current work.

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