

3. THE PRODUCTION OF CARBON NANOTUBE ELECTRON SOURCES

To grow CNTs by PECVD, there are three major requirements: high temperature, plasma and gas. Trying to apply plasma around a heated filament in a chamber fails because plasma requires a large surface area to ignite and be maintained. The surface area around a filament is very small, therefore no plasma forms. Without plasma there is no alignment of the CNTs resulting in poor devices.

The best geometry for stable, strong plasma generation is the parallel plate capacitor, such as that shown in figure 3.1. An even plasma is formed around the stage because of its large, planar surface area.

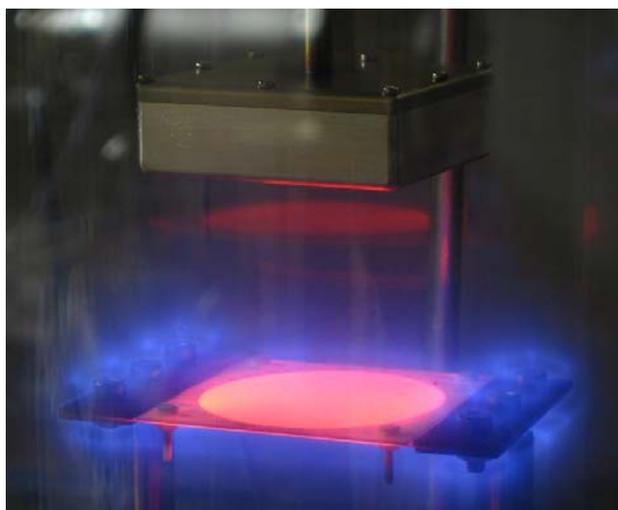


Figure 3.1: Ammonia and acetylene d.c. plasma in a reaction chamber at 2.5 mbar and 700 °C. A strong, stable plasma forms because of the large surface areas of the cathode and anode. Strong plasma relies on large surfaces generating, absorbing and rebounding electrons.

The best way to form CNTs on a tungsten tip would be to somehow incorporate the tips into this heating structure. The rest of this chapter describes how this is done and the results obtained.

3.1 DESIGN OF A CHAMBER TO GROW VERTICALLY ALIGNED CNTS

When applying a potential difference between two parallel plates, approximately all of the voltage applied in the resultant plasma is dropped across the sheath. At the temperatures and pressures commonly used for this process (600-800 °C, 2-5 mbar), the sheath in a plasma extends 2-3 mm above the cathode surface [1]. In order to obtain vertically aligned CNTs, the tip apex needs to sit within this sheath. Figure 3.1.1 shows the design of a stage in which an etched tungsten wire can be held so that the apex of the tip is level with the height of the stage. The specially designed stage involves a flat, planar, conductive heater, such as graphite in the centre of which is a hole of small diameter into which the tip/wire is placed (see fig 3.1.1a), located in the centre of the heater.

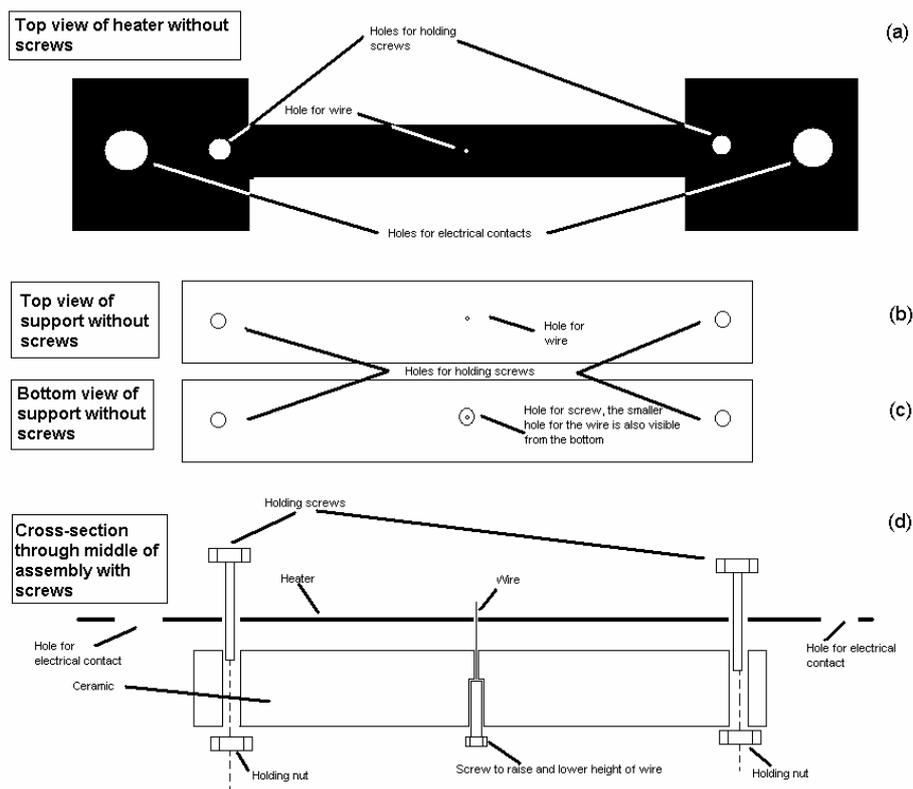


Figure 3.1.1: The sharp wire heater. (a) top view of the graphite heater, (b) top view of the support without screws, (c) bottom view of the support without screws and (d) how the assembly fits together in cross-section. All screw holes are threaded.

The tip/wire is held by a ceramic support (figs 3.1.1b and 3.1.1c), which insulates both heat and electric current. Screws hold the assembly – the heater and the support – together, and the height of the tip/wire can be varied by a third screw located below the tip/wire (fig 3.1.1d).

This new heater holds a number of advantages over the previous method.

- The construction allows chemical reactions on the wire in the presence of high voltage and/or plasma without electric arc discharge because the flat, planar, conductive strip shields the sharp wire from inducing large electric fields at its apex. Without the shielding, the high field magnification causes arcing at the tip destroying any prospect of CNT growth.
- The flat planar strip makes the electric field perpendicular to the plane resulting in vertically aligned growth of nanotubes or nanowires on the wire, which is highly desirable for various applications
- The temperature of the strip can be controlled very precisely ($\sim 1^\circ\text{C}$) by resistive heating, under the flow of reactive gases, which is not the case with current tip/wire-heating methods. Together with this, all of the valves, the flows, the pressure, temperature (with feedback from a thermocouple) and plasma can be controlled by a computer program. This automation has allowed for a much greater control and reproducibility of the process, not to mention the capacity to record all chamber parameters whilst the growth process is taking place.
- The heater is scalable, so many tips/wires can be heated at the same time by adding more holes to the flat planar strip.

Figures 3.1.2a and 3.1.2b show pictures of the stage from above and the side. The stage is narrowed so that the heat is concentrated at the centre of the graphite stage which is where the tungsten wire is situated. This keeps the copper feedthroughs relatively cool. To load the stage, the central upended screw is screwed fully in. The tungsten wire is placed as shown in the sequence of figures 3.1.2c, 3.1.2d and 3.1.2e and then lowered by the central screw so that the apex of the tungsten tip is at the height of the stage.

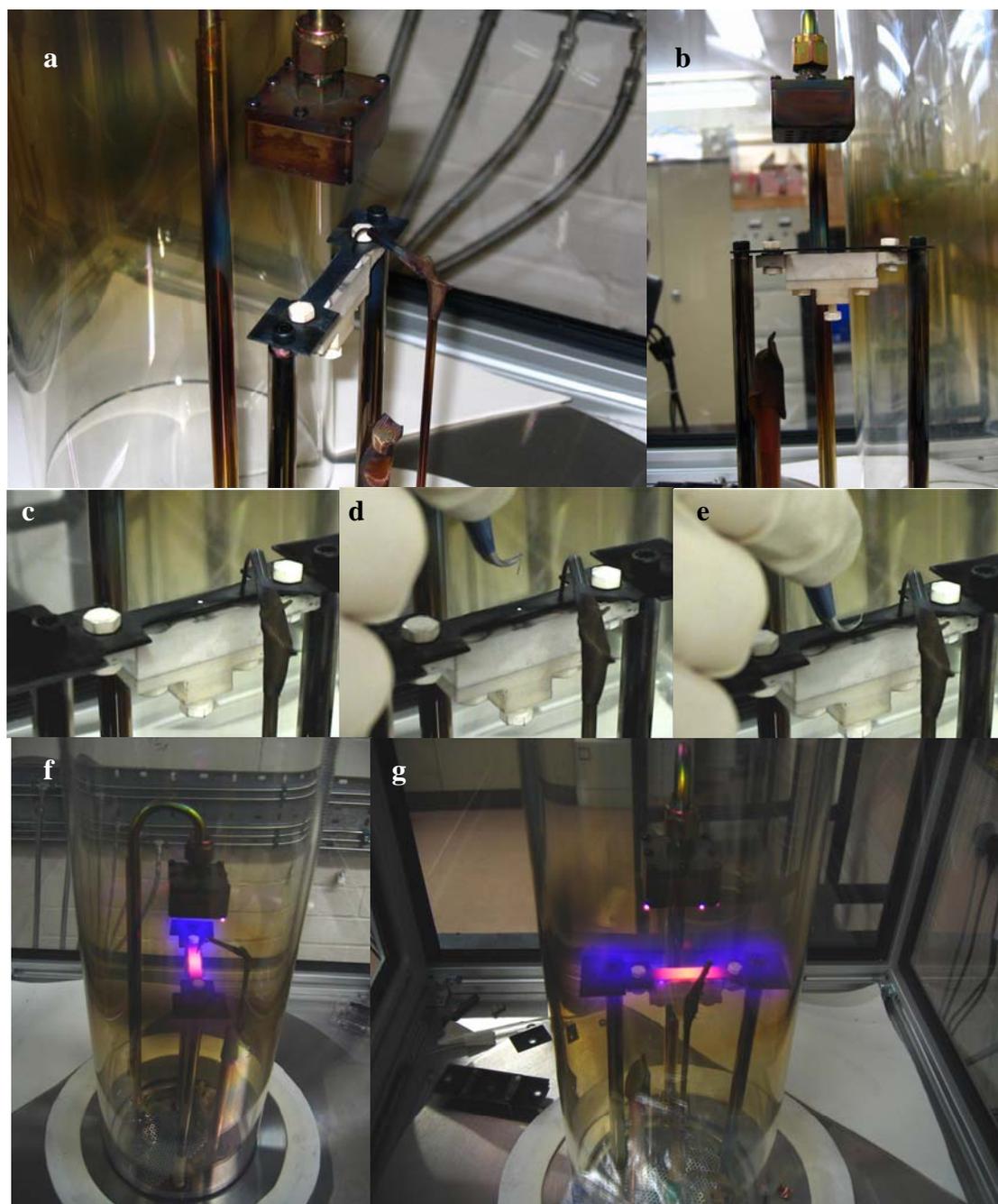


Figure 3.1.2: Modified graphite stage with one hole for tungsten wire growth. a) and b) show different aspects of the stage. Here the stage narrows to concentrate all the heat in the centre of the heater, whilst keeping the copper feedthroughs relatively cool. In figure b), the central upturned ceramic screw is the one that can be used to raise and lower the height of a tungsten wire. The sequence of pictures c) d) and e) shows the mounting procedure of a tungsten wire. The small hole through which the tungsten wire is threaded has been marked by a small grey spot in c) and d). In d), an etched tungsten wire is held by tweezers and is then placed inside the hole in e). Pictures f) and g) show the system during PECVD growth.

3.2 THE EFFECT OF CATALYST ON DIMENSION AND ORIENTATION

Initially, for proof of concept, tungsten tips 125 μm in diameter and approximately 10 mm long were etched to an apex radius of 200 nm. The tips were then placed in a sputter-coater, with their axis aligned perpendicularly to the plane of the sputter target. Approximately 15 nm of ITO was deposited. ITO is required to act as a diffusion barrier, because metal catalyst deposited on a bare polycrystalline tungsten wire will diffuse into the tungsten itself when molten, thus preventing the formation of catalyst particles to nucleate CNT growth. Subsequently, varying thicknesses of either Fe or Ni were deposited by sputtering to determine the most suitable catalyst for CNT growth.

With this setup, limited uniformity of CNT length was obtained using Fe as the catalyst, though diameter was reasonably uniform. Thicknesses of Fe varied from 5-10 nm. Growth was found to be better for smaller thicknesses; CNTs grown at larger thicknesses were short and stumpy, with a large variation in CNT diameter and length. However, even at lower thicknesses, some exhibited large variation in height, with some CNTs grown being 3-4 times the length of neighbouring tubes. Also, some CNTs failed to follow the field lines, whilst others did. A possible explanation for this behaviour is that the growth rate was so fast, that the CNTs' growth direction was determined by differences in carbon feedstock diffusion rates rather than field lines. Typical results are shown in figure 3.2.1.

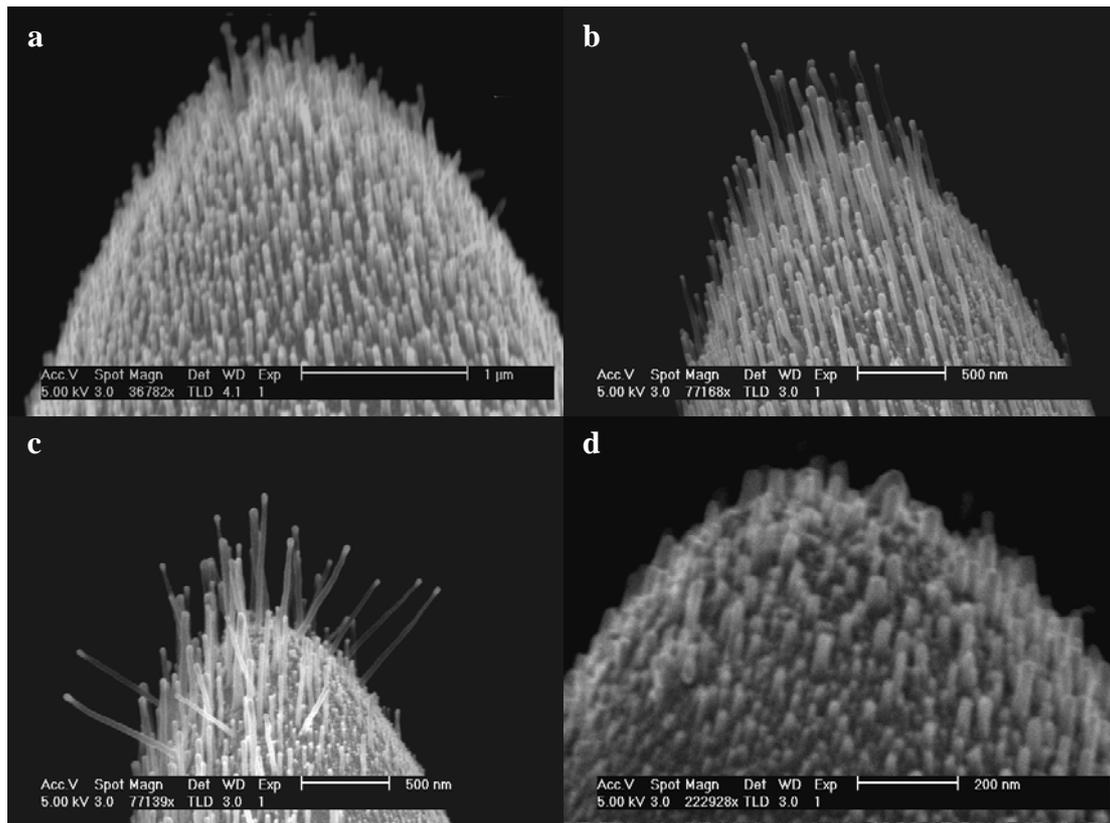


Figure 3.2.1: CNTs grown on tungsten tips with 15 nm ITO and varying thicknesses of Fe catalyst. Each deposition was at 750 °C and lasted for 15 minutes. For (a) the Fe thickness was 5 nm, for (b) and (c) 7 nm and for (d) 10 nm. It can be seen that, there is a large degree of variation and a lack of uniformity in the CNT dimensions. Most CNTs align themselves vertically, but in (c) there it is clear that there is a great variation in alignment and height.

The process was repeated for Ni. Thicknesses of Ni varied from 5-10 nm. Again, thicker layers of Ni resulted in a large distribution of CNT diameters with many CNTs being wider than they were tall. For smaller thicknesses however, the Ni catalysed CNTs exhibited greater uniformity in length and diameter than Fe catalysed CNTs. Most importantly, the grown CNTs aligned vertically with the field. Figure 3.2.2 shows the effectiveness of Ni catalyst. This highly significant result removes one of the key problems of the CNT mounting method used by De Jonge et al [2]. De Jonge's CNTs exhibited poor alignment, with good alignment produced by sheer luck. This process eliminates this uncertainty.

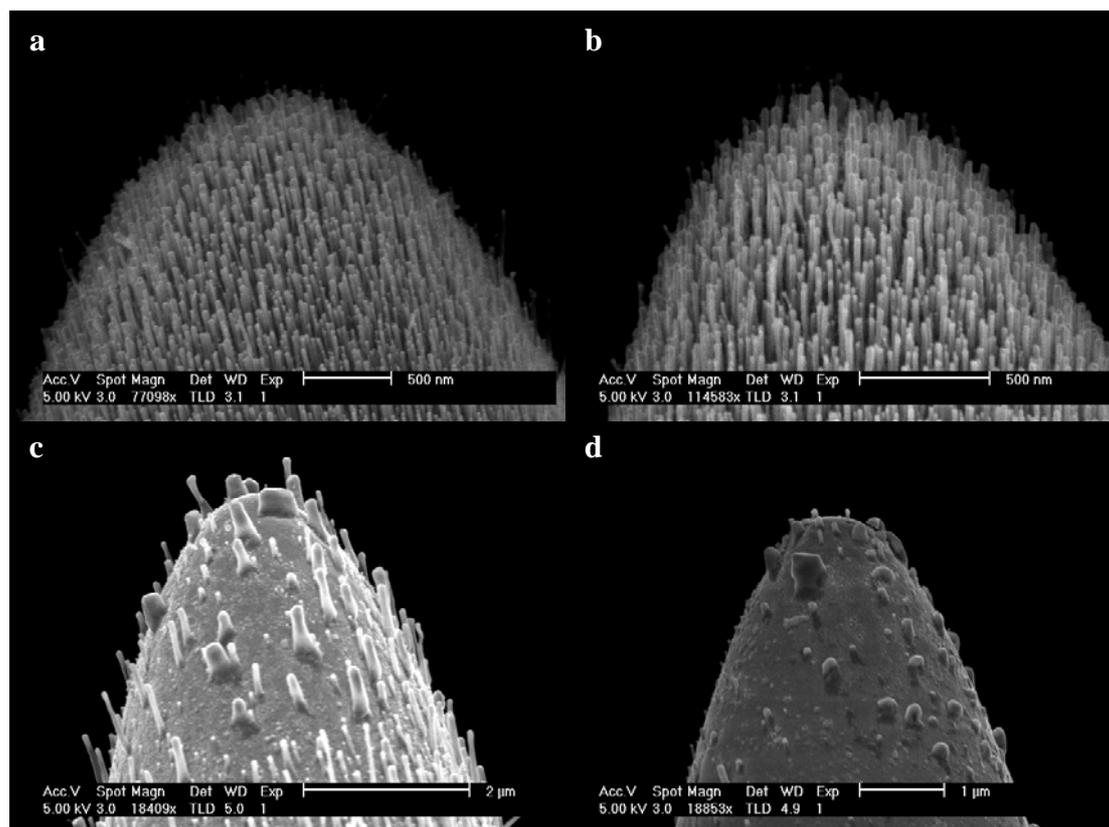


Figure 3.2.2: CNTs grown on etched tungsten with 15 nm ITO and varying thicknesses of Ni as the catalyst. Each deposition was at 750 °C and lasted for 15 minutes. For (a) 5 nm of Ni was deposited, for (b) 7 nm was deposited and for (c) and (d) 10 nm Ni was deposited. The CNTs grown in (a) and (b) show a high degree of alignment, uniformity in dimensions and repeatability. The CNTs also appear ‘straighter,’ i.e. they show fewer deformities that those catalysed by Fe. In (c) and (d), too much catalyst has been deposited, so the Ni coalesces into catalyst particles that are too large for significant or repeatable CNT growth. Ni appears to be a more reliable catalyst. Co was not considered because in the author’s experience it provides poor CNTs for this range of growth parameters.

3.3 GROWING SINGLE CNTS ON TUNGSTEN TIPS

A coherent electron source requires a single source of electrons. Therefore, if CNTs are to be employed as high-quality electron sources, the electron beam should come from only one CNT. This presents a significant problem, because of the difficulty in depositing a small enough amount of catalyst on a 3-dimensional surface so that one

CNT is grown. Among the options considered were: electron beam lithography, focused ion beam lithography, electron beam deposition and electron beam emission.

3.3.1 ELECTRON BEAM LITHOGRAPHY

In this well-established process, a resist is spin-coated onto a surface, dried and exposed to an electron beam. The surface is subjected to a developer which removes the resist that has been exposed to the electron beam. Catalyst is then deposited uniformly across the surface. The remaining resist is then removed, taking the catalyst deposited on top of the resist with it. This leaves behind catalyst deposited directly onto a surface from which carbon nanotubes can grow.

In order for the area of the remaining catalyst to be small enough so that only one CNT would grow, the beam diameter must be small (~100 nm). This is achieved through focusing the electron beam. Wherever the beam is focused, the resist will develop. This is adequate for a silicon chip where focusing can occur far from the active sites and then the chip moved so that the active site is perpendicularly under the now focused beam, thus not altering the focus length. However, on a tungsten tip, we require only one CNT to grow at its apex. There is, therefore, nowhere to focus the beam. There are also problems regarding the deposition of a resist evenly onto a 3-dimensional surface. This is, to say the least, difficult, with the result that this method was discarded.

3.3.2 FOCUSED ION BEAM LITHOGRAPHY

A tungsten tip was coated in 3 films: the first ITO, the second the Ni catalyst, the third an oxide. An ion beam was used to mill through the top-most layer, in the first instance SiO₂, exposing an area of catalyst underneath. Figure 3.3.2 illustrates some of the many problems with this method. Just as with electron beam lithography, the ion beam needs to be focused first. Even if it is focused, the beam then needs to expose the very top of the tip. In figure 3.3.2a, the beam missed the apex and exposed somewhere down the side of the tip. During growth, due to the various stresses in the

thin films, compounded with their different expansion coefficients, the top-most oxide layer cracked, meaning much more catalyst was exposed, resulting in CNT growth on the sides of the tip as well as the top (as shown in figure 3.3.2b). Also, because SiO_2 , which is an insulator, was used as the top-most layer, the tip charged during CNT growth which would eventually result in an electric arc discharge to the tip in most instances, destroying any CNTs that might have grown there. But to detect a transition, you measure a difference in conductance in the beam and the best way to detect a transition is to put an insulating oxide next to a metal to obtain the a good contrast. If this contrast were not there and a conductive oxide or a non-catalysing metal used as a top-layer instead to prevent arcing, it would be almost impossible to determine when to stop milling, which then might continue right through until hitting the tungsten. Figure 3.3.2b shows that despite these drawbacks, a successful, though messy, outcome can result, the number of attempts required to achieve this removes the possibility of using this method for mass production.

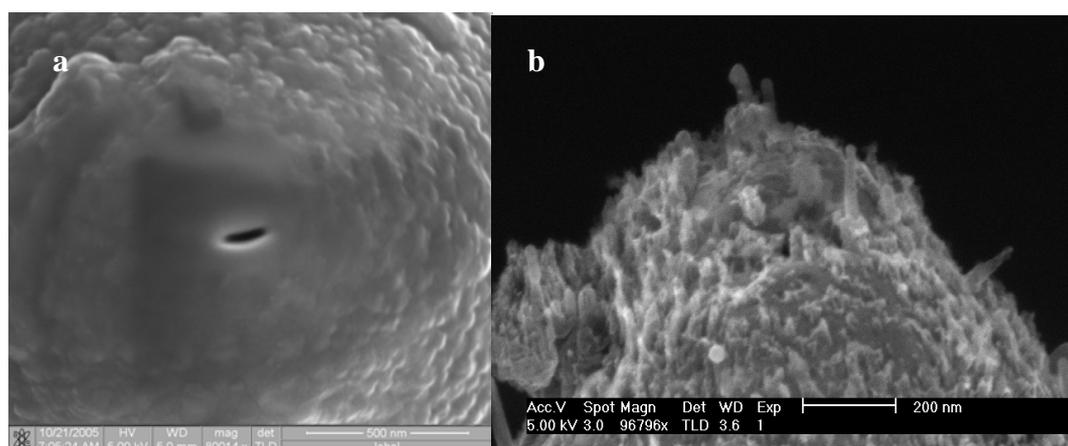


Figure 3.3.2: (a) shows the top view of the result of milling on a tungsten tip covered first in ITO, then 10 nm Ni, then 40 nm SiO_2 . A small hole, seen as the elongated black mark, has been dug on the tip by the process, but has missed the apex (hence the elongated hole), as it is difficult to determine in this image where the apex is. The hole is also 150 nm across, so this would probably result in the growth of two CNTs. (b) shows the growth of two CNTs at the top of a tungsten wire with this process. Further CNTs have grown further down due to cracking of the oxide layer.

3.3.3 ELECTRON BEAM DEPOSITION

The premise of this method is to inlet a gas such as ferrocene or nickelocene into an electron microscope and deposit directly the amount of catalyst onto the apex of a tungsten tip. Whilst it is now possible to focus the electron beam as there is no lithographical step, it is very difficult and awkward to deposit such small quantities of catalyst in this way and in the correct position. One questions whether it would be any quicker or better than the method already used by de Jonge et al [3]. Also, modifying an electron microscope in this way is expensive and is quite out of the question for university research.

3.3.4 ELECTRON BEAM EMISSION

The most abstract of the proposed solutions, electron beam emission involves depositing resist onto a tip, then using the tip to field emit, developing the resist with electrons from the tip rather than an outside source. Whilst at first this sounds like an elegant solution, it turns out to be the trickiest of all. The elegance comes from the fact that the field emission will come from the tip's sharpest point, the apex, thus self aligning where a CNT could grow. However, every tip is different, especially as they are polycrystalline. They will have different work functions and slightly different geometries, which together results in the turn-on voltage being different for each tip. This is a significant problem when one realises that the time required to develop the resist is in the order of milliseconds. This, coupled with the problem of depositing resist evenly on a 3-dimensional surface again eliminates this method as a viable option.

3.3.5 GEOMETRIC MANIPULATION

Ultimately, lithography will fail because it is almost impossible to focus the beam in the right spot. Lithography is also energy and time consuming and is unlikely to offer a significant improvement on simply sticking CNTs to tips. The best method will entirely avoid the use of lithography.

It is possible to etch tungsten wires to a radius as small as 20 nm. They are unstable for field emission at this size which is why such tips are not used as field emission sources themselves. Their shape is similar to a circus tent roof but stretched in the vertical direction (see figure 3.3.5a). It results in a very high aspect ratio between the sides of the tip and its radius towards the apex. The structure at the very tip is much like that of a church spire (as in figure 3.3.5b).

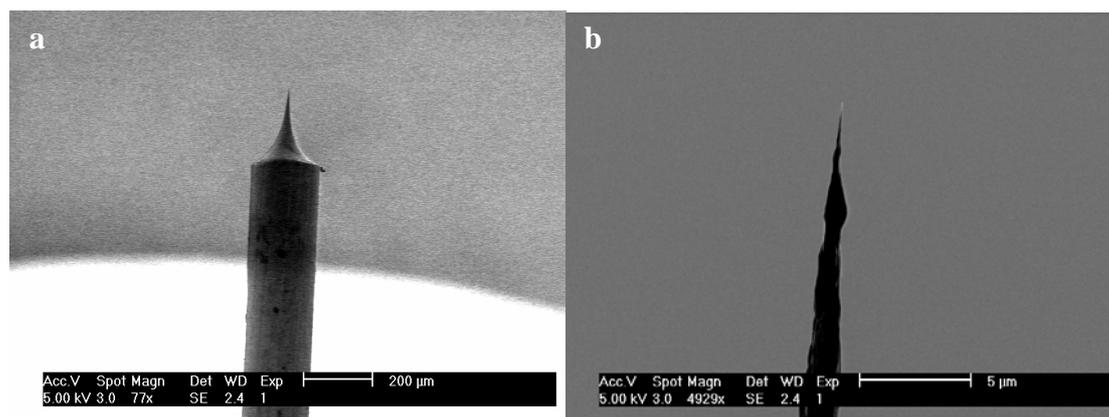


Figure 3.3.5: (a) shows the profile of a tip at low magnification. The tip is 150 μm in diameter. (b) is the tip at higher magnification. Note the steep sides of the tip and the sharpness of the apex.

With the tungsten wire etched to such a small radius, if ITO and Ni were deposited all over the tip, it is possible that there would only be space for just one CNT to grow at the apex. There is only room for one Lord Nelson on his column! In theory, there is nowhere for the CNT to nucleate on the side of the tip, so there would be one CNT grown at the top of the tip, with the next CNT growing much further down. The question is, if this were put inside a chamber for field emission testing, would the field on the CNT closest to the apex, but not on it, be small enough so that only the CNT grown on the very apex emits?

3.4 ELECTROSTATIC FIELD SIMULATIONS FOR MULTI-CNT TIPS

Before embarking on field simulations, it is important to determine the behaviour of Fowler-Nordheim emission. Figure 3.4.1 shows the I-V plot from a CNT grown by the author which will be described in greater detail in chapter 4. It shows how the total

current increases exponentially with increasing voltage. Since total currents of more than $1\ \mu\text{A}$ are not required and voltage is proportional to field for this geometry, it is safe to conclude that secondary CNTs whose fields are less than half of that of the primary CNT will not field emit.

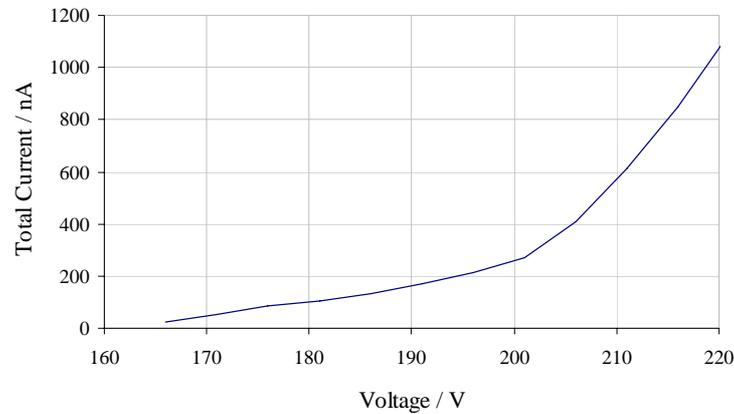


Figure 3.4.1: Field emission from a CNT grown by the author. The current increases exponentially with voltage over a very narrow voltage range. Total currents of $1\ \mu\text{A}$ are more than sufficient for the electron beam in an electron microscope in this instance.

COMSOL Multiphysics © was used to simulate the fields around the primary CNT at the apex of a tungsten tip, and around a secondary CNT further down the tungsten tip. More than one secondary CNT will reduce their respective contribution due to field shielding effects, so an isolated secondary represents the highest risk of multi-CNT emission and is consequently the only geometry simulated here. The geometry simulated was two CNTs of identical dimensions with the position of the secondary CNT on the tip being variable. The geometry mimicked the dimensions of an electron source module with an extractor and suppressor. The field units were arbitrary, since we are only interested in the field at the apex of the primary CNT relative to that of the secondary. Figure 3.4.2 shows a typical simulation where the secondary CNT is positioned down the tungsten shaft at a distance 1.5 times the height of the primary CNT's.

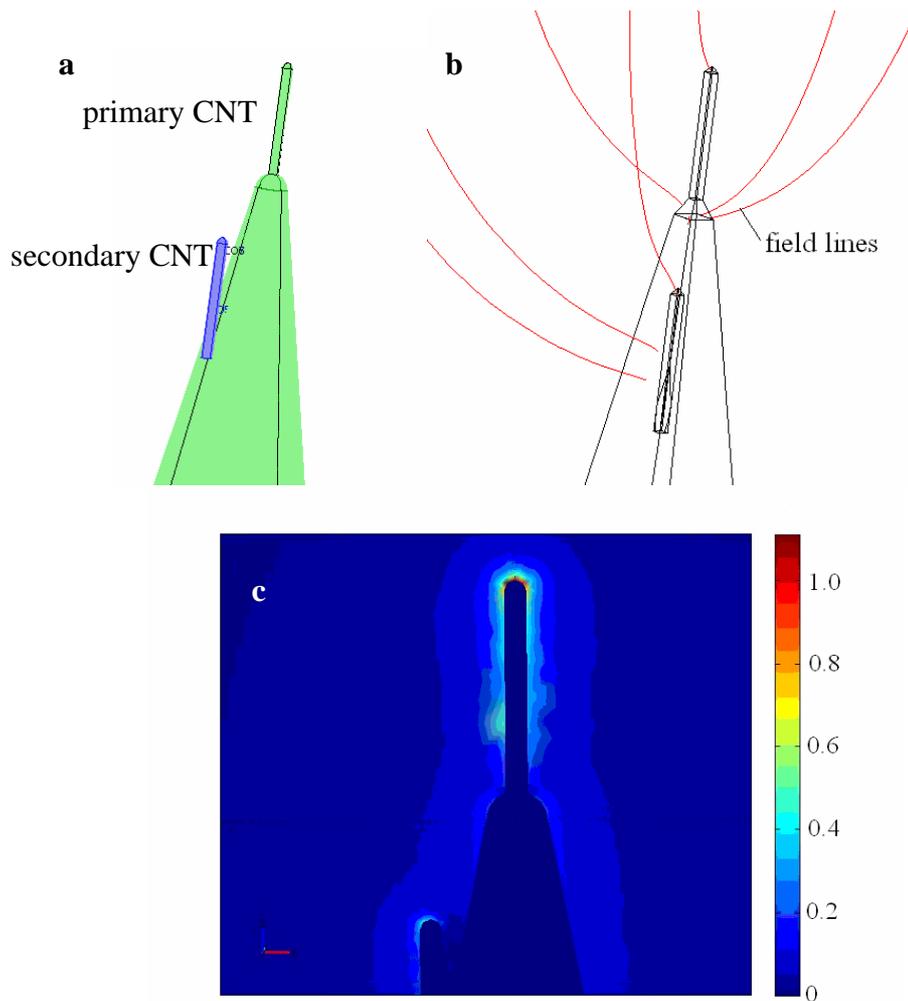


Figure 3.4.2: (a) shows the geometry simulated. Here the secondary CNT (in blue) is positioned 1.5 times the length of the primary CNT (in green) down the tungsten tip. Both CNTs have the same dimensions. (b) shows a 3-dimensional solution with some field lines, and (c) is a cross-section that maps the field size around the CNT. The field units are normalized about the maximum located at the CNT apex. The red areas indicate the highest field, and these unsurprisingly are around the apex of the primary CNT. The field around the apex of the secondary CNT is much smaller, in this case, about a third of that at the top.

It was found that the point at which secondary CNTs at the apex become a concern is when one nucleates half the length of the primary CNT down the shaft of the tip. If the secondary CNT nucleates below this point, its likelihood of contribution to the electron beam is negligible since the local field at the apex becomes less than half that of the primary CNT. Table 3.4 summarizes the key results of these simulations.

Table 3.4: A summary of the results of simulations of electrostatic field strength at the apex of secondary CNTs grown further down tungsten tips.

| Distance of nucleation point as a proportion of the height of the primary CNT | Magnitude of field at the apex of secondary CNT as a fraction of the field at the apex of the primary CNT |
|---|---|
| 0.25 | 0.66 |
| 0.5 | 0.50 |
| 1.0 | 0.42 |
| 1.5 | 0.32 |
| 2.5 | 0.18 |

The simulations suggest that even if a CNT did grow on the tungsten tip quite close to its apex, it would still be unlikely to emit. Consequently, the challenges are to etch tungsten wire to small radii with a repeatable method and to deposit catalyst on the tip in such a way that only one CNT will grow there.

3.5 REPRODUCIBILITY OF TUNGSTEN WIRE ETCHING

A key factor in the repeatability of the CNT grown is the precision with which the tungsten wire can be etched, because the diameter of the CNT will be controlled by the amount of catalyst deposited on the tip. An Omicron tip etching control unit was used to regulate the current passed through the tip during electrolysis. The setup is illustrated in figure 3.5.1 and was carried out at Philips Research Laboratories (PRL), Eindhoven, The Netherlands. The threshold voltage was set to ALPHA, the etching voltage set to BETA, and the sensitivity set to GAMMA. The cut-off current was 6 mA. One end of a 10 mm tungsten wire was submerged 2 mm below the surface of a beaker of 5 M KOH_(aq). Etching of the tungsten wire would take approximately one minute. Figure 3.5.2 shows the distribution of 25 etched tungsten tip radii. The radii follow a roughly normal distribution, with a mean of 52 ± 3 nm and a first standard deviation of 17 nm, which is 33% of the mean value.



Figure 3.5.1: Left shows the stand used to hold the tungsten wire. A graduated screw is used to lower the tungsten wire, held by a long, steel clamp, to 2 mm below the etching solution meniscus. Right, the power pack used to regulate the current during electrolysis.

Assuming a typical catalyst thickness and that the catalyst forms into a ball for CNT growth, this would result in a variation of 21% in the CNT diameter which is five times the variation of 4.1% reported by Teo et al. [4] who grew CNTs on a flat surface. Polycrystalline tungsten was used for this etching method because it is much cheaper than single crystal tungsten, whose dimensionality can be much better controlled through etching.

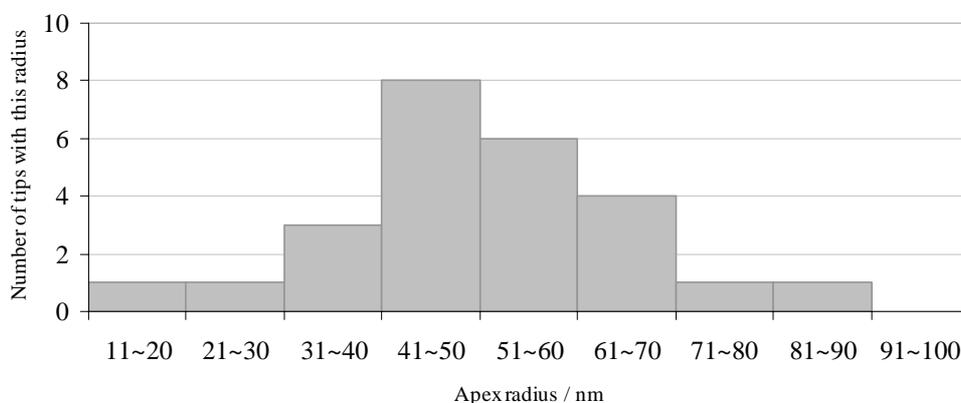


Figure 3.5.2: Distribution of tungsten tip radii for a sample of 25. The standard deviation of tungsten radii is 17 nm which is 33% of the mean of 52 nm.

3.6 OPTIMIZING CATALYST DEPOSITION

The catalyst is deposited as a thin film on a surface of high curvature. It is therefore important to find a deposition method that gives the most precise and uniform film in order to exert maximum control over the CNT dimensions. Two methods were available for catalyst deposition: sputtering and evaporation. The latter was investigated first.

3.6.1 CATALYST DEPOSITION BY EVAPORATION

Growth of CNTs on small-radius W wire proved more difficult to control when the catalyst was deposited by evaporation. Ni evaporated tended to agglomerate at the apex often resulting in the tip having a globular, wavy structure at the end (see figure 3.6.1.1). This is probably a result of the type of evaporator used (a BOC Edwards E380) in which both the tip and source are stationary. In more advanced evaporators, the samples are rotated to give an even coating. However, given the short deposition time, it is unlikely that this would make much difference. Indeed, a second, one-off system with a rotating sample holder at Applied Physics Technologies Ltd., McMinnville, Oregon, yielded similar results.

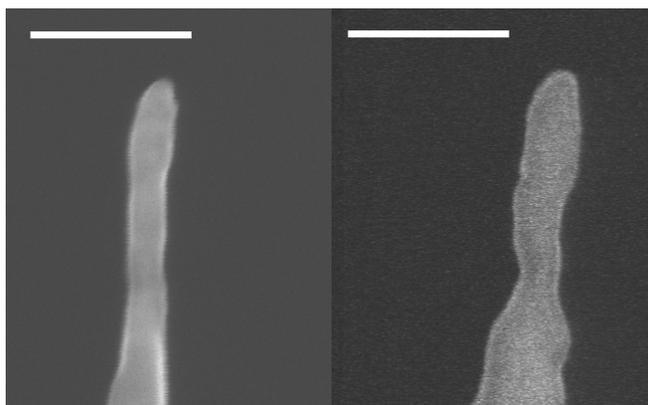


Fig. 3.6.1.1. W tip before (left) and after (right) Ni evaporation. ITO has already been deposited. The scale bar is 200 nm. The tip has clearly grown but in a non-uniform way, with more catalyst forming in some areas than others. Such deposition will not result in repeatable results.

The tips were placed in specially developed sample holder 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 NH₃ inlet at 120 sccm, raising the pressure to 3.4 mbar. Upon reaching 750 °C, C₂H₂ 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 25 minutes, producing CNTs of various dimensions.

Despite deposition difficulties, the amount of catalyst deposited was often small enough for single 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 more frequent larger catalyst deposits. 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 figure 3.6.1.2).

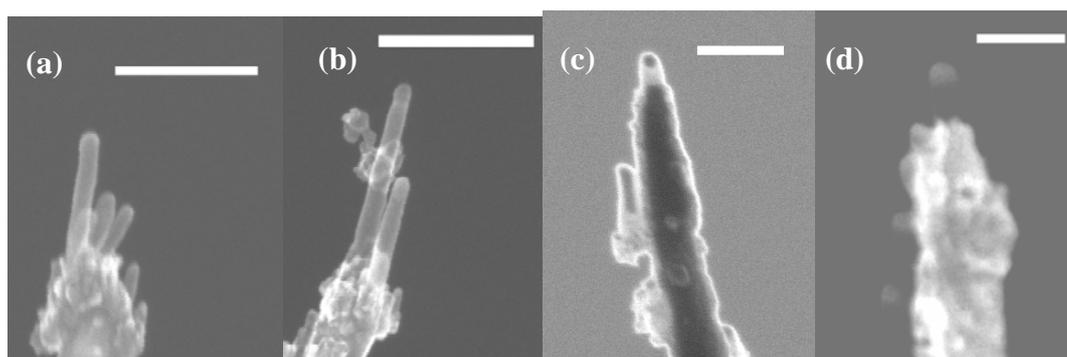


Fig. 3.6.1.2. (a) and (b) show multiple CNTs grown at the apex of sharp W tips, (c) and (d) show single CNTs grown at the apex of sharp W tips. The scale bar is 200 nm. Ni catalyst particles can clearly be seen in the bottom last two images. The Ni catalyst was deposited by evaporation.

For single CNTs grown at the apex, the diameter is controlled by the radius of the apex. As a rule of thumb, the CNT diameter is approximately equal to the radius of the apex. This method yielded a single CNT tip yield of approximately 20%. Evaporation was abandoned as it was considered to be unreliable.

3.6.2 CATALYST DEPOSITION BY SPUTTER COATING

Sputter coating was thought to offer a more precise deposition method because the deposition rate is smaller and can be controlled more accurately. Following coating by ITO in the sputter coater, the tips were kept in position with their axes aligned perpendicularly to the plane of the sputter target and a 5 nm layer of Ni deposited.

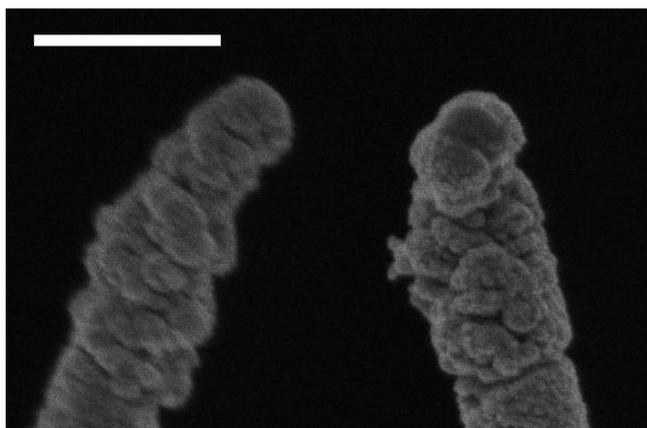


Fig. 3.6.2.1. W tip before (left) and after (right) Ni sputter coating. ITO has already been deposited. The scale bar is 200 nm. The tip has clearly grown but in a more uniform manner than by evaporation. This method is much more promising for catalyst deposition.

Ni catalyst deposited by sputter coating provided much more reliable results (as seen in figure 3.6.2.1). The films deposited by sputter coating tended to produce more precise results due to the slower deposition rate compared with that used in the evaporator. Sputter coating also gave a more uniform coating around the tip than evaporation which exhibited extra accumulation around the tip apex and where the exact angle at which the tip is mounted is more critical to the uniformity of the coating (figure 3.6.1.1). 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 CNT at the tip is isolated from the others at the base and on the application of a voltage will generate a much higher field than the

others at the base with resultant field emission only coming from those CNTs at the tip.

Again, the tips were ramped to 750 °C at 300 °C/min and NH₃ inlet at 120 sccm, raising the pressure to 3.4 mbar. Upon reaching 750 °C, C₂H₂ was inlet at 30 sccm, raising the total pressure to 4.5 mbar as before. A potential of 640 V was again applied between the showerhead and stage with 25 minutes of growth, producing CNTs of various heights and radii (figure 3.6.2.2).

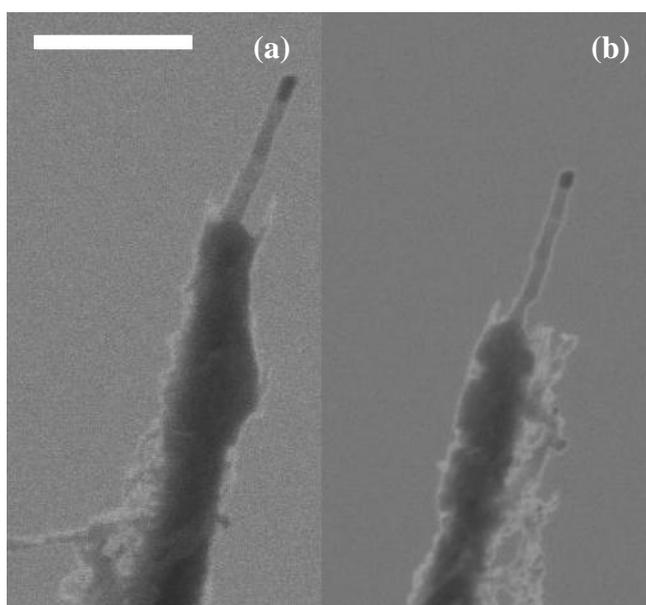


Fig. 3.6.2.2: (a) and (b) show single CNTs grown at the apex of sharp W tips. The scale bar is 200 nm. Ni catalyst particles can clearly be seen at the top of the CNTs. The Ni catalyst was deposited by sputter coating. Note that the CNTs are aligned with the axis of the tip.

Due to the increased uniformity of catalyst coating, the yield of single CNTs was found to be much higher. The next section will detail statistical analysis of CNTs grown by this method.

3.7 STATISTICAL ANALYSIS OF CNTS GROWN ON SHARP TUNGSTEN TIPS

A statistical analysis was performed on 90 tungsten tips used to grow CNTs by this method. The statistics include tips that were broken during the manufacturing process, tips that were etched to too large a diameter for single CNT growth and tips that were hit by an electric arc discharge during growth.

3.7.1 YIELD OF SINGLE CNT TIPS PRODUCED

Of the 90 tips, 44 produced single CNT tips. A single tip was defined as one where the apex of the top-most secondary CNT was below the position at which the primary CNT nucleated. Figure 3.7.1 explains this definition in more detail.

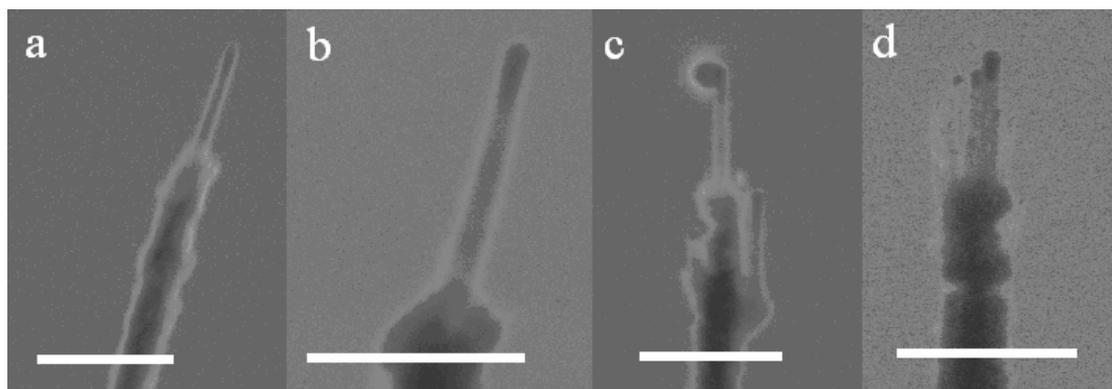


Figure 3.7.1: A selection of CNTs grown on tungsten tips. (a) and (b) show single CNTs on tips, (c) shows a tip with one CNT at the apex (with a bit of amorphous carbon on it which is removed by either heating or field emission) and a secondary CNT some way down the shaft of the tip. As the secondary CNT's apex in (c) is below the level at which the primary CNT nucleates, this is defined as a single CNT tip. (d) shows multiple CNTs at the apex and this is not counted as a single tip. The scale bar is 500 nm in each image.

This gives a yield of 49%. Considering how cheap polycrystalline tungsten is compared to single crystal tungsten and also considering the time and effort it takes to produce an aligned CNT by the de Jonge method, this is a significant result. With

fine-tuning, it is conceivable that this figure could reach and even go beyond the 70% yield of quality Schottky tips sold by FEI Company.

Also, considering this process has been designed so that it can be scaled up to mass production (see later), electron source manufacturers could select which tips to keep and which to reject at little significant extra cost.

3.7.2 DISTRIBUTION OF CNT RADII

The amount of Ni deposited by sputter coating was kept constant at 7 nm and the growth parameters were also kept constant. The diameter distribution of forty-four single tips were analysed. Figure 3.7.2.1 shows the distribution of CNT diameters.

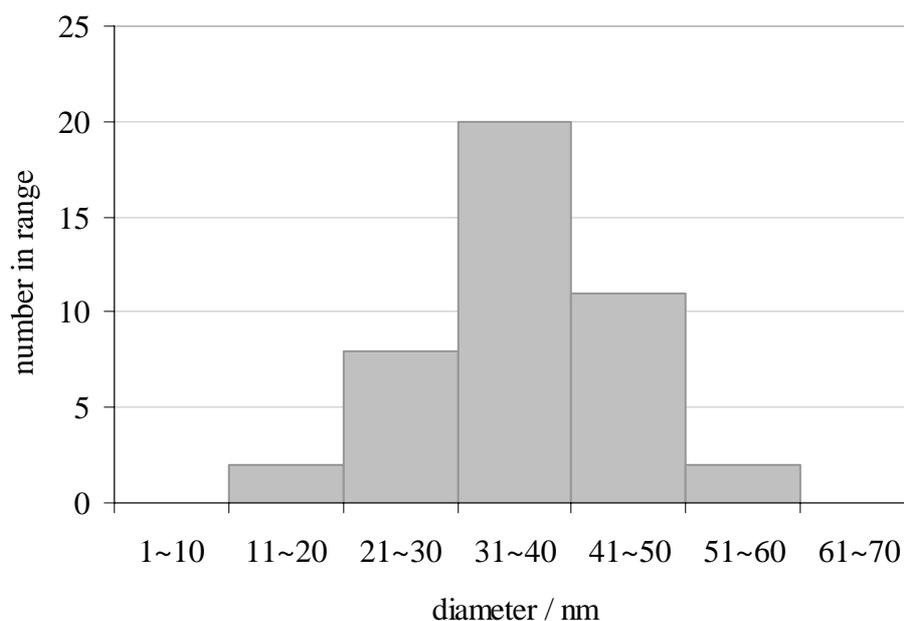


Figure 3.7.2.1: Distribution of CNT diameters for constant catalyst thicknesses and growth parameters. The distribution is roughly Gaussian with a mean diameter of 37 ± 1 nm and a standard deviation of 7 nm which is 20% of the mean.

The mean diameter was found to be 37 ± 1 nm with a standard deviation of 7 nm, 20% of the mean. This is roughly the same standard deviation predicted from the variation

in the radius of the tungsten at its apex. If the deviation in the radius of the tungsten tip was the dominant cause of deviation in the CNT diameter, one would expect a correlation between the volume of catalyst and surface area at the tungsten tip apex. A graph plotting this data is shown in figure 3.7.2.2.

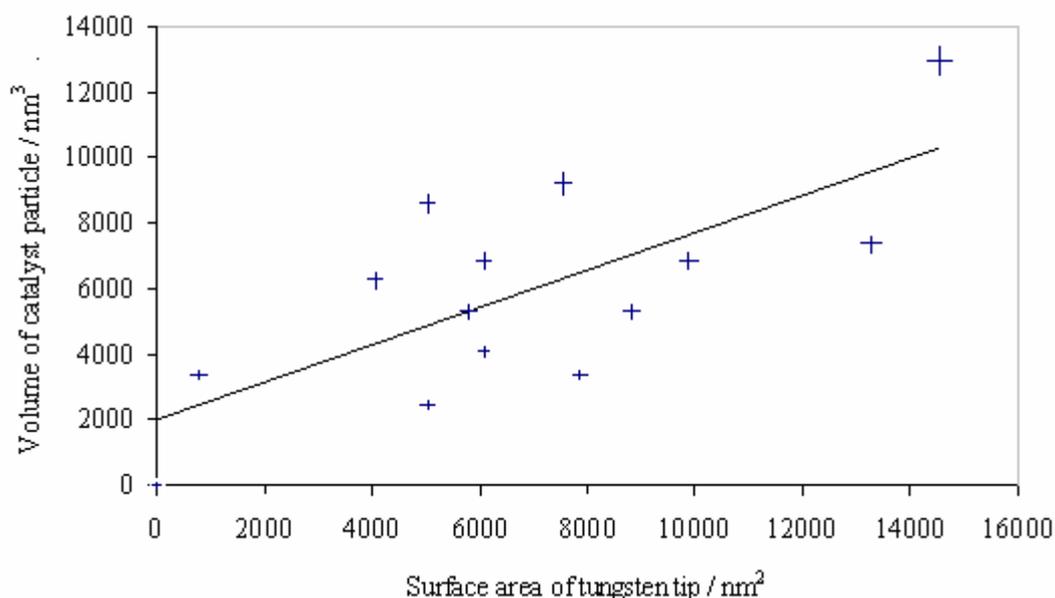


Figure 3.7.2.2: Graph plotting the correlation of surface area of the tungsten tip with the volume of the catalyst particle. The catalyst particle is assumed to be spherical. The correlation is rough at best.

Figure 3.7.2.2 indicates that there is little correlation of tungsten surface area and the resultant volume of catalyst particle. Whilst there is a general trend, it must be concluded that other factors are responsible for CNT diameter variation, as well as the variation in tungsten apex radius.

3.7.3 VARIATION IN CNT LENGTH

For CNTs grown with identically deposited catalyst thicknesses together with identical growth processes, one would expect the length not to deviate at all and be proportional to only growth time. However, growth time is not the only factor that affects CNT length. If the catalyst particle is very small (~20 nm in diameter), only a limited amount of reactant species can diffuse through or around the catalyst particle.

If the catalyst particle is large (~60 nm in diameter), more feedstock is required to build larger CNT walls. Consequently, there is a catalyst size which gives the optimum growth rate. The diameter of the CNT is proportional to the diameter of the catalyst particle. The optimum catalyst size would depend on temperature, gas concentration, plasma parameters, but since all of these are kept constant, one might expect to see a peak in the growth rate, providing that the diameters deposited were small enough to obtain the optimum growth rate.

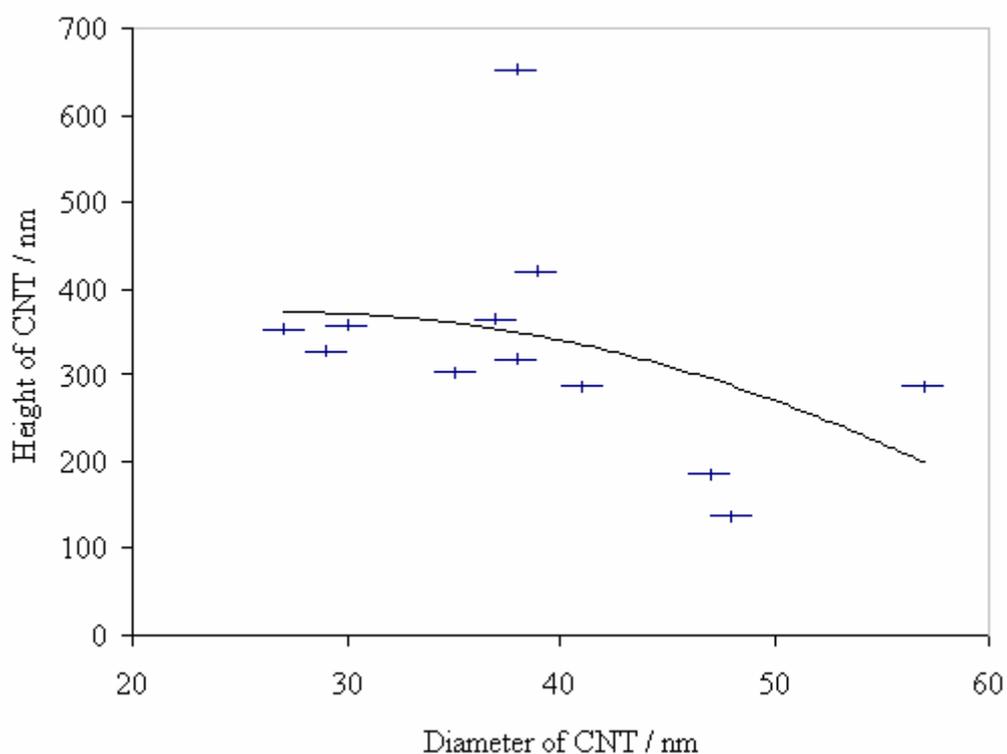


Figure 3.7.3: Variation of height of CNT with diameter of CNT. There is a rough correlation where growth rate tails off for larger CNTs which is mainly due to the increased surface area required to build the CNT. CNTs of lower diameters exhibit greater uniformity in height.

No peak growth rate was observed, with the data shown in figure 3.7.3. This suggests that the optimum growth rate for these conditions was less than 30 nm or simply that the effect is not pronounced. Some CNTs produced were unusually long (such as the one 655 nm in height) and some CNTs of larger diameter did not follow the trend (such as the CNT 57 nm in diameter), so the variation about the mean in height of 355 nm is 125 nm (35%) if the wild CNTs are included, or 80 nm if they are not (23%).

This is significantly worse than the 6.3% quoted by Teo et al. (3) for flat substrate growth. The growth rate is therefore 14 ± 3 nm/min.

3.7.4 ALIGNMENT OF CNTS GROWN ON TUNGSTEN TIPS

It was a stated desire at the start that to minimise astigmatism, the CNT grown must be aligned on the axis of the tungsten wire so that the beam emanating from the CNT would come out as straight and central as possible.

Due to the nature of the tungsten etch, towards the apex the wire bends slightly. Also, some CNTs grown were of an insufficient size to measure the angle with which they grew to the field direction precisely. Consequently, 23 tips were selected to perform a statistical analysis of growth direction. Their growth direction was measured with respect to the axis of the tip. Figure 3.7.4.1 shows how the growth angle varies.

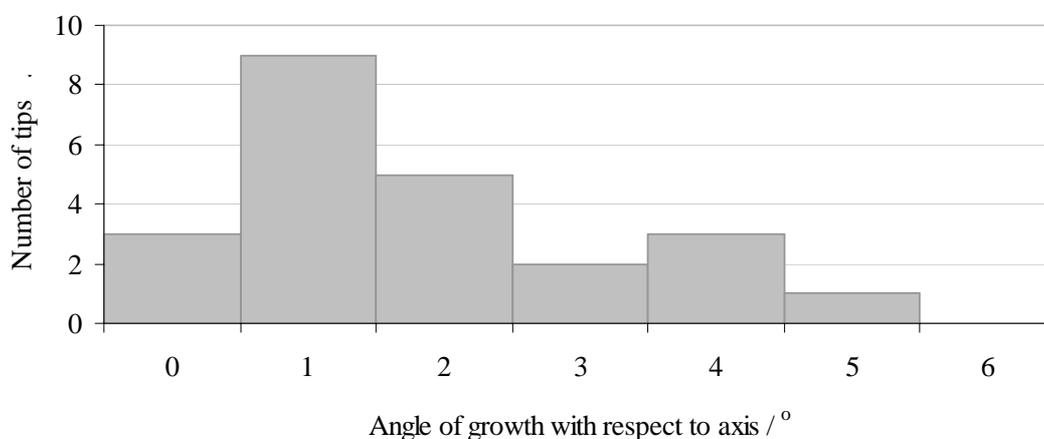


Figure 3.7.4.1: Distribution of growth angle with respect to the axis of the tungsten tip. No tip was found to grow more than 5° from the tungsten axis. All measurements were made to the nearest degree.

CNTs grew at an average of $1.8 \pm 0.3^\circ$ to the tungsten axis. Poor alignment is probably due to how the tungsten wire is placed in the growth stage. Because the hole through which the wire is placed is slightly wider than the diameter of the wire, there is room for the wire to decline from the vertical. This is illustrated in figure 3.7.4.2. Whilst the

growth direction aligns with the field, the field might not necessarily be aligned with the tip resulting in growth at a small angle to the wire's axis. A more precise stage would reduce the variation in growth angle. Despite this, the relatively small angular distribution is significantly lower than the De Jonge method [3] and the electrophoresis method [5] of 6° mentioned in chapter 2.

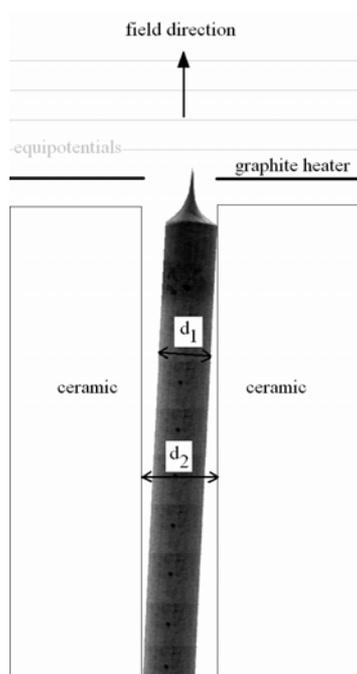


Figure 3.7.4.2: A schematic diagram showing how a tungsten wire placed in the ceramic holder beneath the heater stage could produce off-axis growth of CNTs on the tungsten wires. The angular distribution can be reduced by reducing d_2 to a size closer to d_1 .

3.7.5 DISCUSSION OF POSSIBLE FLUCTUATION CAUSES

There are a number of factors that cause the CNT growth to be less precise than that found in flat substrate growth. The precision with which the tips were etched was as bad as the precision with which the CNTs grew. The tip of each tungsten wire was different in structure each time, which determines how each catalyst particle de-wets. It was also very difficult to keep constant the height to which the tungsten tips were lowered. If all tips were uniform, it would be much more straightforward to design the stage in such a way that the support retracts by the same amount each time. Subtle

differences in height will change the temperature at the tip, the amount which protrudes into the plasma and the amount of CNT that could be etched away by the plasma as it grows. These factors can be controlled with investment.

3.8 GROWTH OF CNTS ON SINGLE CRYSTAL TUNGSTEN TIPS

Some single crystal tungsten wire was made available to the author and the process repeated for comparison with one main difference being that there was no requirement for ITO deposition, because there are no crystal planes for the nickel catalyst to diffuse down. This would theoretically reduce the resistance at the tungsten-CNT interface as there is no oxide there, which improves conductivity and thus opens up the possibility of using these tips for Scanning Tunnelling Microscopy (STM).

Obviously due to expense, there is not enough data to carry out satisfactory statistical analysis, but a general trend can be observed. The first thing to note is that the appearance of the tips is very different. When Ni is deposited, there is more likely to be a coating on the sides of the tip. Surface physics studies the interactions of atoms with crystalline surfaces. Ni was found to form in islands when deposited by evaporation or by sputter coating [6] onto single crystal surfaces such as tungsten with regular spacing. This phenomenon is observed here, with CNTs growing down the tip (see figure 3.8). Although only 12 tips were grown, with 6 of them single CNT tips, a greater uniformity was observed in height and diameter, though this could be due to chance. This however would be an expensive means of increasing uniformity.

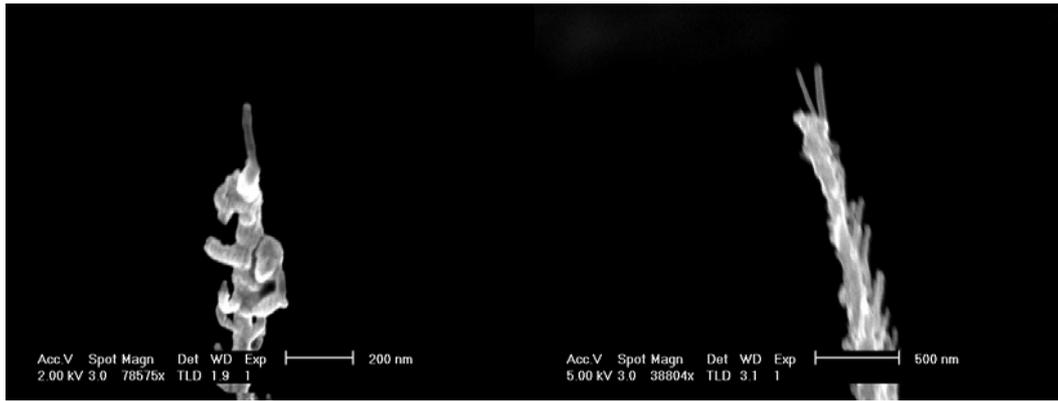


Figure 3.8: Growth of CNTs on single crystal tungsten tips. Left shows a single CNT, right, a double tip. CNTs grown on single crystal showed greater uniformity but also increased CNT growth around the sides.

3.9 CRYSTALLINITY OF CNTS

Minoux et al. [7] showed that the maximum current that can be obtained from a CNT can be greatly enhanced through post-growth treatment by rapid, thermal annealing. CNTs grown by PECVD contain more 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 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 ($\sim 10^{-6}$ mBar). This process of annealing to improve the graphitisation 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 recently discovered process can be successfully applied to carbon nanotubes on tungsten tips

was carried out. Tests have indeed shown that there is a distinct improvement in the crystallinity of CNTs subjected to 1100 °C for 6 mins at an initial pressure of 3×10^{-6} mBar as shown in figure 3.9.1.

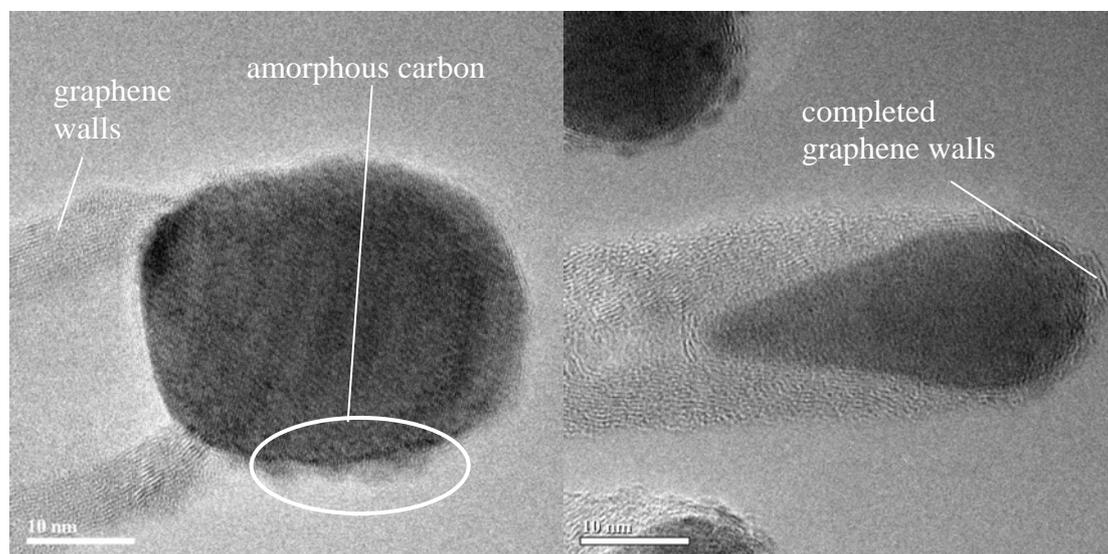


Figure 3.9.1: *Left*, TEM micrograph of the cap of a typical CNT grown from Ni catalyst at 750 °C. Note the disordered and amorphous cap structure without the wall-like graphene structure observed further down. *Right*, shows a CNT that has been annealed for 6 mins at 1100 °C and 3×10^{-6} mBar. Graphene structure is clearly visible all the way around the cap, though the walls are wavy. However, there is clearly a marked improvement in the CNT as a consequence of the annealing process.

The level of graphitization is clearly improved post-annealing because the applied heat has enabled carbon dissolved in the catalyst to diffuse out to form graphitic carbon, completing the cap structure. The structure of the wall of the CNT is also improved with this process, giving energy to complete outer walls, strengthening the CNT and making it more conductive (see figure 3.9.2). From field emission measurements (detailed in chapter 4) the difference that annealing makes to the field emission pattern, the emission stability and the brightness of the source is clear. A full characterisation of this will be provided in chapter 4.

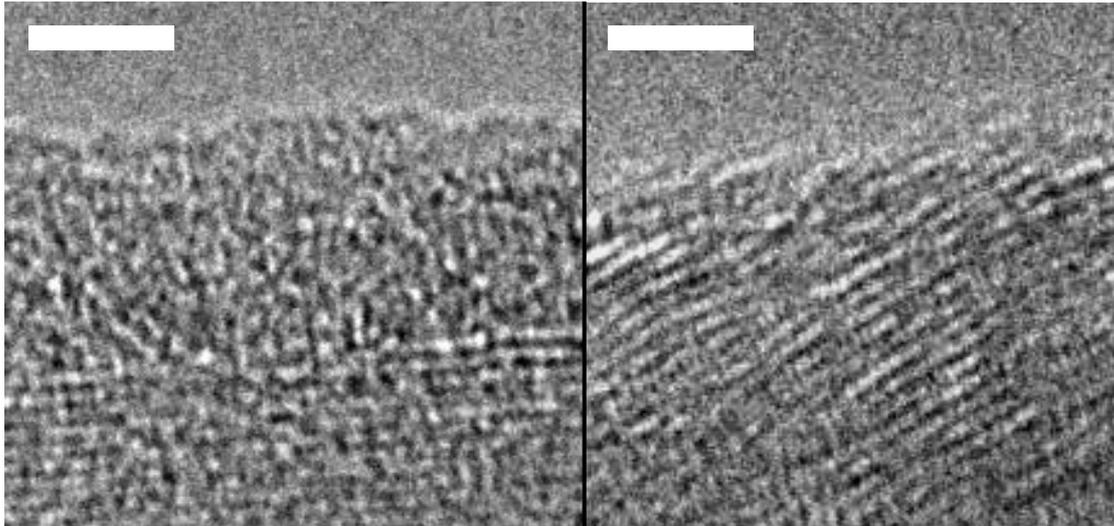


Figure 3.9.2: Left shows a TEM electron micrograph of a CNT pre-annealing. The graphene walls can be seen on the inside of the tube (bottom), but this is covered by an amorphous carbon layer (top). Post annealing, right, the outer graphene walls are completed and amorphous carbon removed. The scale bar is 2 nm in each.

3.10 MODIFYING THE PRODUCTION PROCESS

In order to mass-produce CNT electron sources, it is necessary to make many sources at the same time. The first improvement to the production process was to increase the number of tungsten wires placed in the reaction chamber per process from one to four. Space restricted this being increased any further, but as shown in figure 3.10, if the heater were to be increased further in size, there is nothing to stop the parallel processing to increase enable the production of to twenty, fifty or more simultaneously, as the heat is distributed uniformly between all the tungsten wires in the heater.

To obtain some field emission data, especially energy spread data, the alignment of the tungsten and the CNTs is critical (the problems in obtaining this data will be expanded upon in chapter 4). To mount tungsten wire with grown CNTs, the wire was spot-welded to a Schottky base. The growth process makes the tungsten brittle, so once spot-welded, the tungsten cannot be bent for alignment. Consequently, most CNTs mounted this way gave no energy spread data.

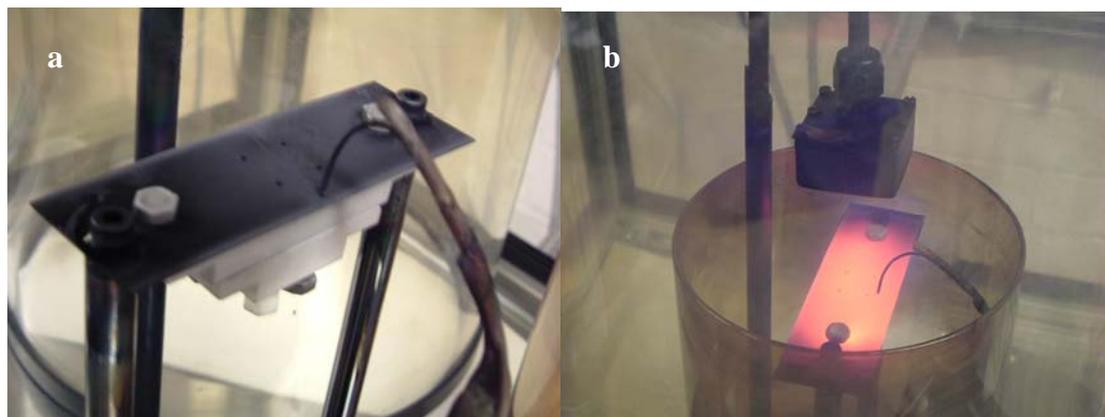


Figure 3.10: Growth stage modified to accommodate four tungsten tips. In a), four holes can be clearly seen and are symmetrically located about the centre point so that they all experience the same temperature and plasma conditions. This is evident in (b) where the colour of the graphite heater is symmetrical about the centre.

To solve this problem, two approaches were applied. The first was to etch a tungsten wire already attached to a specially designed mount, the second to place an entire, already aligned electron source into the PECVD reaction chamber.

3.10.1 GROWTH ON SPECIALLY DESIGNED MOUNTS

It was soon realised that whilst the CNTs were aligned very accurately on the tip, the tip itself was not aligned. Therefore, to get the energy spread data required, a modification had to be made to the mounting process. The first modification attempted was the use of a machine (see figure 3.10.1.1a) based at Philips Research Laboratories, Eindhoven, The Netherlands, where tungsten wires were spot-welded to a U-shaped mounting pin (figure 3.10.1.1b) which is used to heat the tungsten wire. This system allowed for movement in all dimensions, and crucially, offered rotation, which gives almost unlimited freedom in trying to align a field emission bright spot.

A new ceramic holder was made that allowed the mounting pin to be manoeuvred through a small hole in the graphite stage. The mounting pin, was then subjected to the usual PE-CVD growth process seen in figures 3.10.1.1c and 3.10.1.1d.

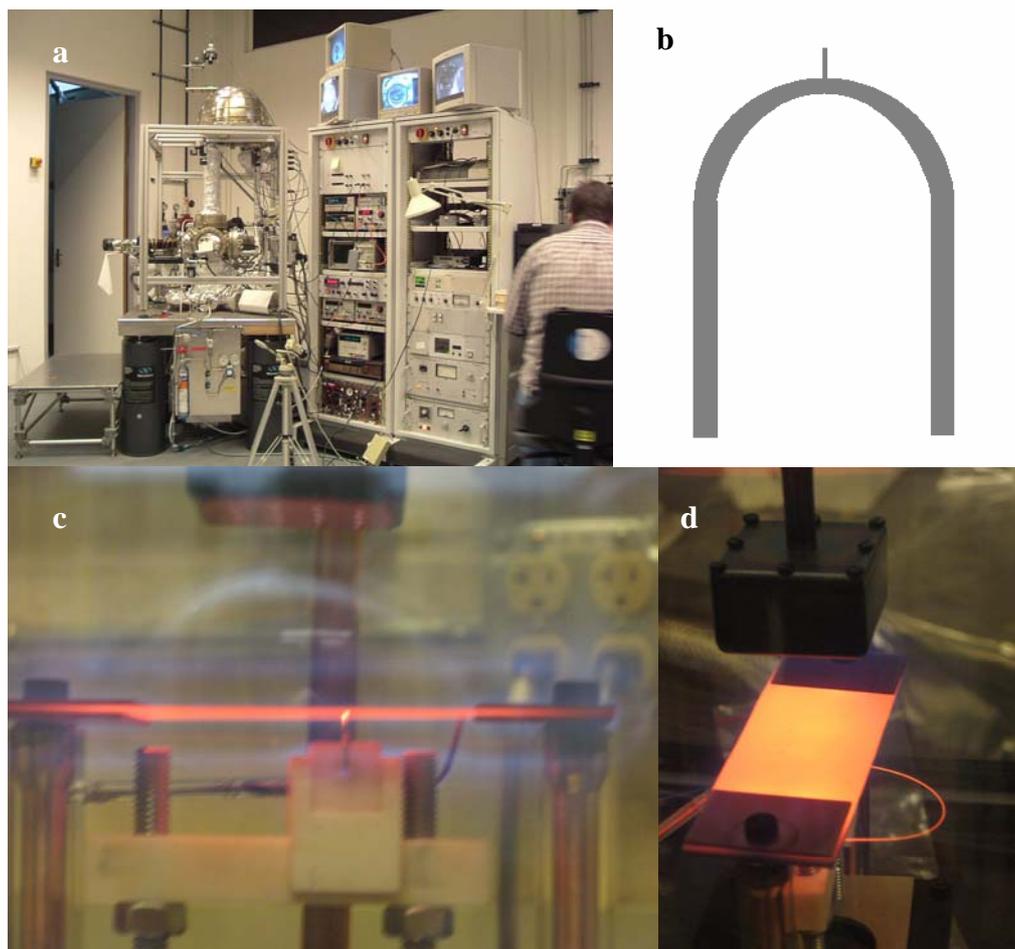


Figure 3.10.1.1: (a) shows the system used for energy spread measurements, (b) the mounting pin used in the growth. The etched polycrystalline tungsten wire is the short thin protruding wire at the top. (c) and (d) show the mounting pin during the PECVD process. The plasma can be clearly seen in (c). The mounting pin is either kept in contact with the stage (c) or has a small tungsten wire running to it to keep it at the same potential as the stage (d).

Only a small number of CNTs on tips were made this way: just enough to get the required energy spread data. CNTs grown with this modified method still exhibited the same characteristics of those grown onto single tungsten wires as can be seen in figure 3.10.1.2.

Some of the etched tungsten tips were slightly bent at the apex, but interestingly, the CNT still grew in the vertical direction. This can be seen in figure 3.10.1.3. In PECVD, CNTs follow field lines during growth, which means that the field shielding caused by the large, flat, graphite heater has a significant effect.

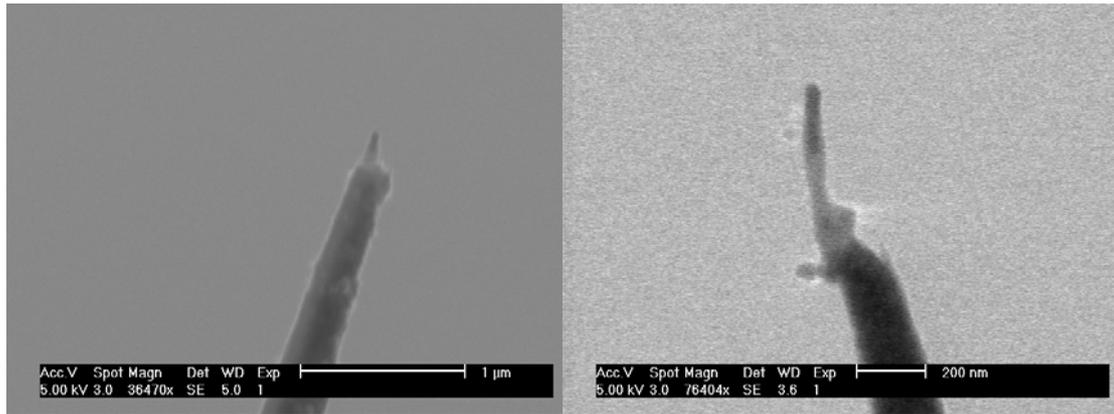


Figure E: Two CNTs grown by PECVD on a mounting tip. The CNTs show similar dimensions and structure to those grown on single tungsten wires.

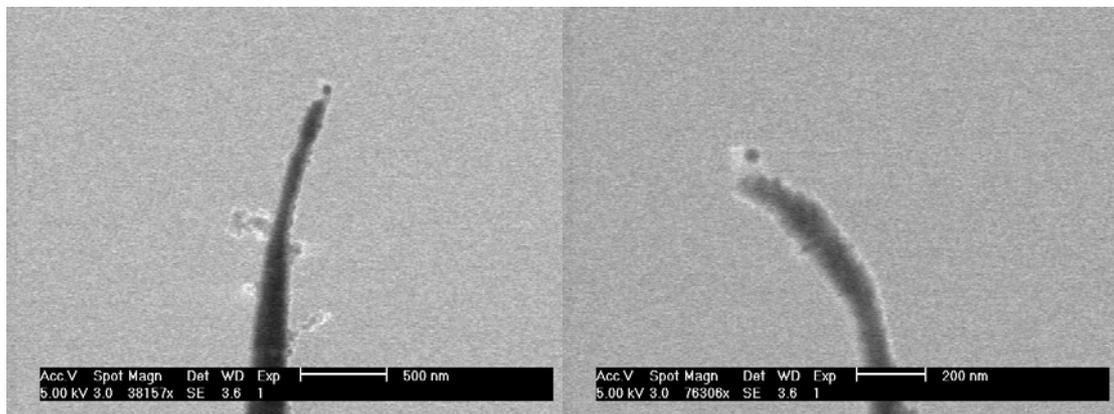


Figure D: Two CNTs grown on bent tungsten tips. The CNTs still grow in the vertical direction despite the fact that the tip is bent.

It is clear that this method need not only be applied to growing CNTs on tips. It can be applied to growing a limited amount of CNTs on a wide array of 3-dimensional structures. All that is required is a hole in the graphite heater of an appropriate size.

3.10.2 GROWTH ON WHOLE ELECTRON SOURCES

In manufacturing electron sources, a number of tricks are used to bring the alignment of electron sources down to less than 25 μm from their desired position. All this becomes much more difficult when trying to manipulate a brittle tungsten wire rather than a malleable single crystal tungsten wire. Given that off-the-shelf electron sources

are all aligned correctly, it makes sense to see whether the whole module can be placed inside the reaction chamber to give the optimum alignment of a CNT electron source.

Tungsten wires were attached to a Schottky base first, then etched, then mounted in a suppressor module from York Probe Sources Ltd. The structure of this module can be seen in figure 3.10.2.1.

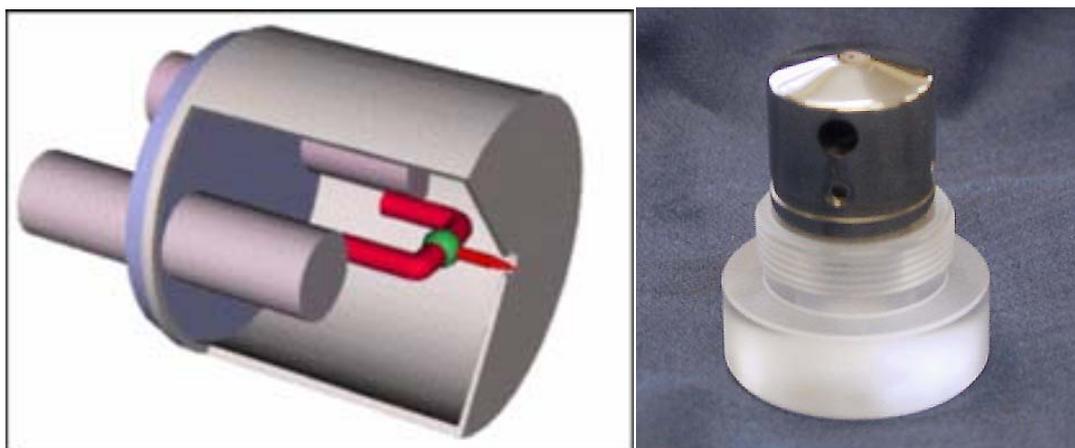


Figure 3.10.2.1: *Left*, a schematic diagram of the electron source module. The tungsten needle, on top of which the CNT is grown, is seen protruding through the suppressor. *Right*, a photograph of the electron gun sitting on a quartz stand. These electron sources were subjected to PECVD for CNT growth.

The tungsten tip protrudes a few hundred microns from the suppressor as in normal electron sources. To complete the electron gun, an extractor is inserted over the top of the suppressor, but this is not used here. The tungsten wire used was again polycrystalline.

The whole source was placed inside a sputter coater and coated with 15 nm ITO and 7 nm Ni. A new graphite stage and ceramic holder were made for PECVD growth. The ceramic holder held the feet of the Schottky base which was free to move vertically on two large ceramic rods. At the bottom of the rods were ceramic feet which could be moved relative to the stage, thus giving room for manoeuvre in the other two dimensions. The stage was specially designed so that heat would be uniformly distributed around it. The cross sectional area was the same throughout, so that the

resistance would be the same everywhere and thus the heat generated by electric current passing through. In the centre of the stage, a 10 mm hole was cut. This setup can be seen in figure 3.10.2.2.

When placed in the stage setup, the Schottky base was shorted to the suppressor to prevent a potential difference occurring between the tip and the suppressor. This was done by attaching a short piece of wire. For growth, the suppressor was pushed up to the graphite stage along the ceramic rods so that it was in physical contact with it. The source was positioned such that the tungsten tip was in the centre of the 10 mm hole.



Figure 3.10.2.2: Two pictures of the electron source module inside the growth chamber. The graphite stage has a 10 mm hole in the centre, so the stage is wider around the module to keep the cross-sectional area perpendicular to current flow constant and the temperature uniform across the heater. The electron source stands on a ceramic support which is free to move up and down two ceramic rods, which in turn are free to move relative to the stage. In this case a piece of copper tape has been used to short the suppressor and tungsten tip. The suppressor is pushed up against the stage to make electrical contact.

The growth recipe was modified slightly. The tips were ramped to 750 °C at 300 °C/min and NH₃ inlet at 120 sccm, raising the pressure to 3.4 mbar. When the stage reached 750 °C, it was held at this temperature for 5 minutes to allow the whole electron source to reach this temperature. From experience, if the plasma is applied too early, the plasma will break down to the cold suppressor surface, destroying the tip. After 5 minutes passed, the C₂H₂ 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 source to initiate the plasma. Plasma covered the tip and the source module and was observed inside the module itself (see figure 3.10.2.3). The growth was performed for 25 minutes.



Figure 3.10.2.3: Left shows the source during growth. The plasma can be seen glowing around the whole source. Right shows the source after growth. Due to the different thermal expansion coefficients, the grub screws have worked loose resulting in the tungsten tip protruding further above the suppressor than before. As the suppressor is to be replaced by a new one, this is not a problem. The suppressor's function is to protect the tip structure and alignment within.

In this reaction chamber, there was only enough room to deposit on one module at a time. There is no reason again why the process cannot be scaled up for larger reactors so that more modules can be processed in parallel. Modules should be processed in parallel because the process takes roughly twice as long as the single tungsten wire process due to the longer heating cycle and the length of time it takes to cool down (~30-45 mins) giving a total time of 1 hr 15 mins per cycle compared to 35 mins for

the single tungsten wire process. During the process, the grub screws holding the module together work free. This is probably due to a difference in the thermal expansion coefficients of tungsten and the ceramic to which they are attached. The grub screws attach the suppressor to the ceramic Schottky base and a result of the screws slackening is the suppressor sinks so that the tungsten tip protrudes further from the suppressor than before the process started (see figure 3.10.2.3). But because the whole electron source module was placed in the sputter coater for catalyst deposition, the result is CNTs covering the whole suppressor. The suppressor-tip module is a 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.

Each electron source costs approximately £200 thus reducing the number of times this experiment can be carried out, so again, only a limited amount of statistics can be employed here. A similar success rate to single tungsten tips was achieved with tips grown in modules. Figure 3.10.2.4 shows a few single CNT tips.

Of the 28 electron sources made most recently by this method, 13 yielded single CNT tips. This gives a success rate of 46% which is close to the 49% obtained from the tungsten wire experiments. The dimensions of the CNTs grown were similar to previous processes, with diameters ranging from 30-55 nm and heights varying from 250-500 nm. 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 to bring CNT electron sources to market in the very near future.

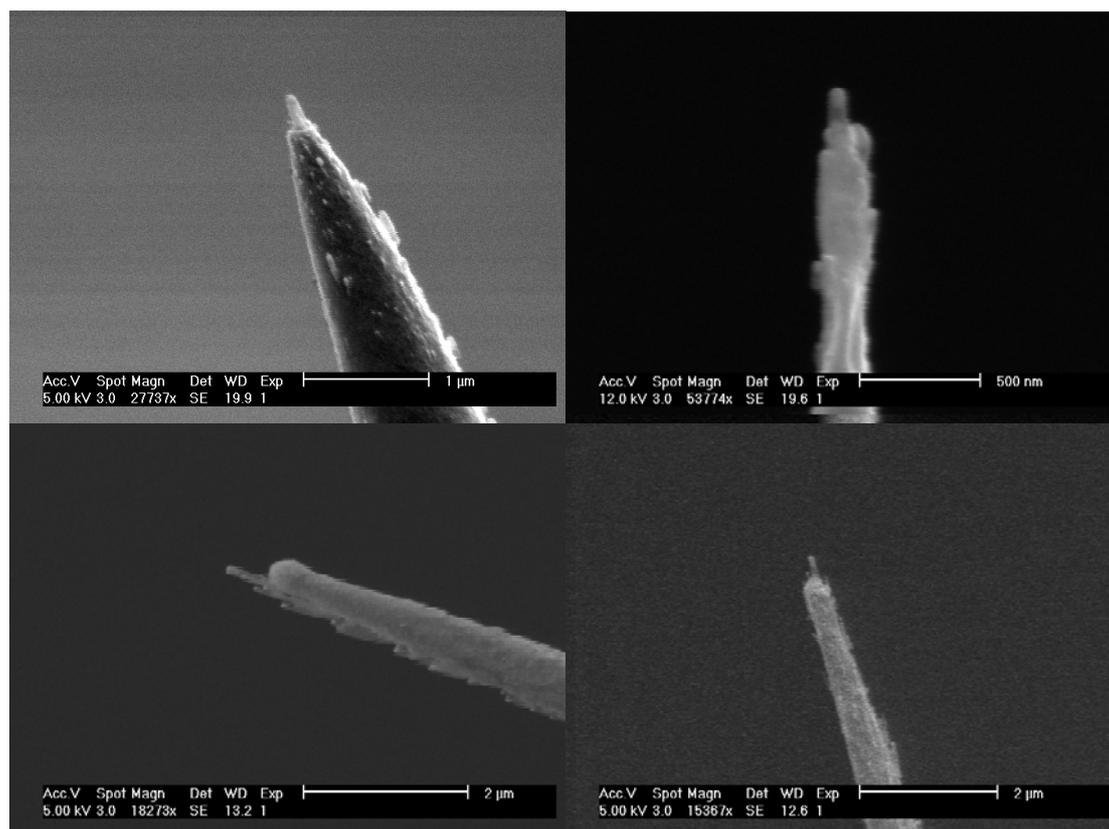


Figure 3.10.2.4: Four single CNTs grown on tungsten tips mounted in electron sources. The dimensions and success rate are similar to the process used to grow CNTs on single pieces of polycrystalline tungsten wire.

3.11 HANDLING OF TIPS

Objects of small dimensions are prone to electrostatic discharge (ESD). It is precisely because the field enhancement factor is so high for CNT tip structures that they are particularly prone to this phenomenon. ESD occurs when a small amount of charge is built up in an object. The charge dissipates through the object's sharpest point when either brought into contact with something (much like an electric shock one experiences on a hand rail) or if the charge and field combined is high enough, when brought into contact with air. A simple experiment was carried out to examine the effect of ESD on CNT tips. Figure 3.11.1 shows the before and after of two poor quality tips. The tips were imaged in the SEM. They were then removed from the SEM by a pair of tweezers, taken on a 10 metre walk whilst being held by the

tweezers and then returned to the SEM for imaging. The result is the disappearance of the CNTs and leaving a burnt, blunter tip behind. This is typical of ESD.

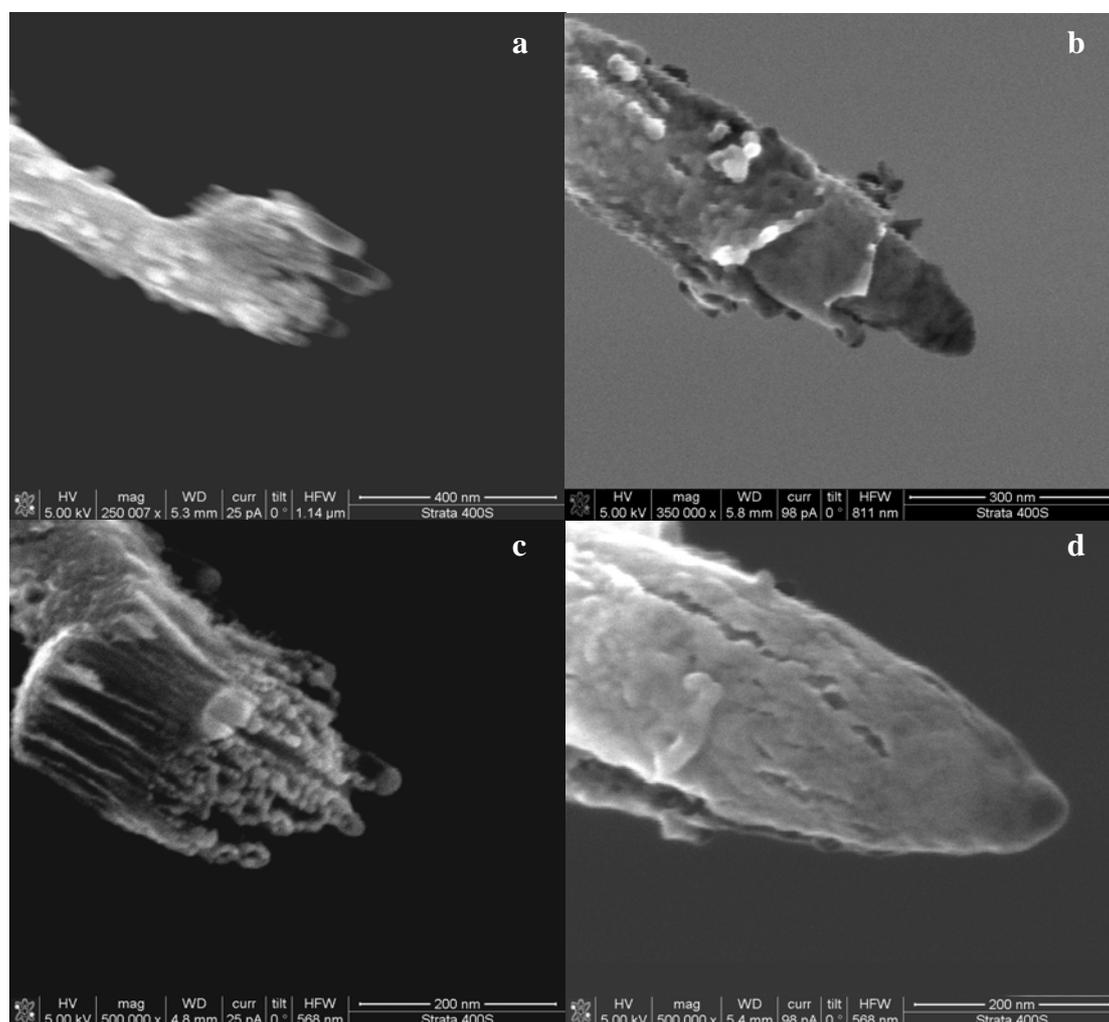


Figure 3.11.1: Two tips before and after ESD experiments. (a) shows a tip in the SEM, (b) the same tip after being removed from the SEM, taken for a short walk around the room then placed back in the SEM for imaging. The CNTs at the tip have disappeared with what appears to be slightly burnt remnants. (c) and (d) tell the same story. This is typical of ESD.

Whilst this may appear catastrophic, in reality, simple safeguards are all that are required to prevent this from happening. Objects inside metal boxes are protected from external electric fields. Consequently, in order to transport these tips over any distance, they should be stored inside metal container such as that shown in figure 3.11.2. Also, whilst handling tips, both the tip and the tip handler should be grounded. An earthing strap is sufficient and is standard practice for people operating within this

field. Finally, current spikes should be avoided when switching the tips on. However, this is something that will be tackled in the next chapter.

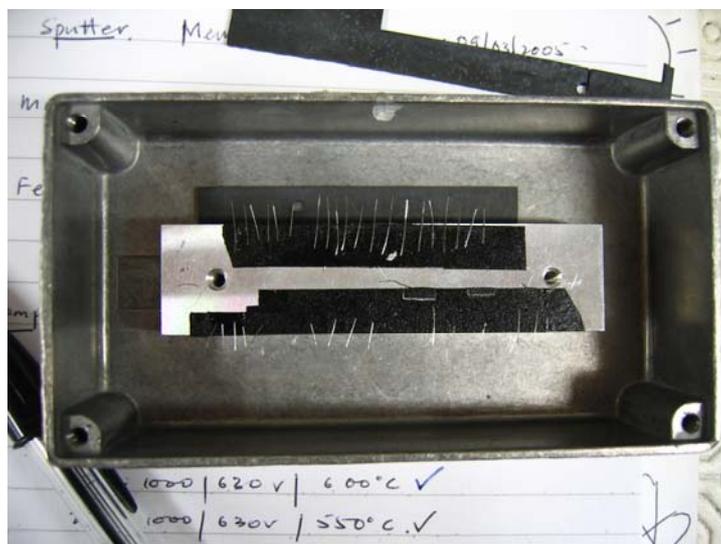


Figure 3.11.2: Tungsten wires on which CNTs have been grown prepared for transportation. The wires are stuck to sticky carbon tape, incidentally the same as that which De Jonge used to attach his CNTs to etched tungsten wires for his measurements. A lid screws on the top and provided that the handler and box is earthed, no CNTs are lost from tip apexes during transportation.

3.12 LIFETIME AND ROBUSTNESS

Of the wires transported across the Atlantic using the De Jonge method, very few survive. This suggests that the method used to attach CNTs is insufficient for long-lifetime tips. At the very least, the degree to which the CNTs are stuck to the tip varies enormously.

All CNT tips produced by the growth method survive transportation across large distances and rough handling. CNTs don't fall off which is indicative of a strong bond between the CNT and its substrate. The CNTs can survive temperatures up to and including 1200 °C and survive weeks of varied field emission tests (as in figure 3.12).

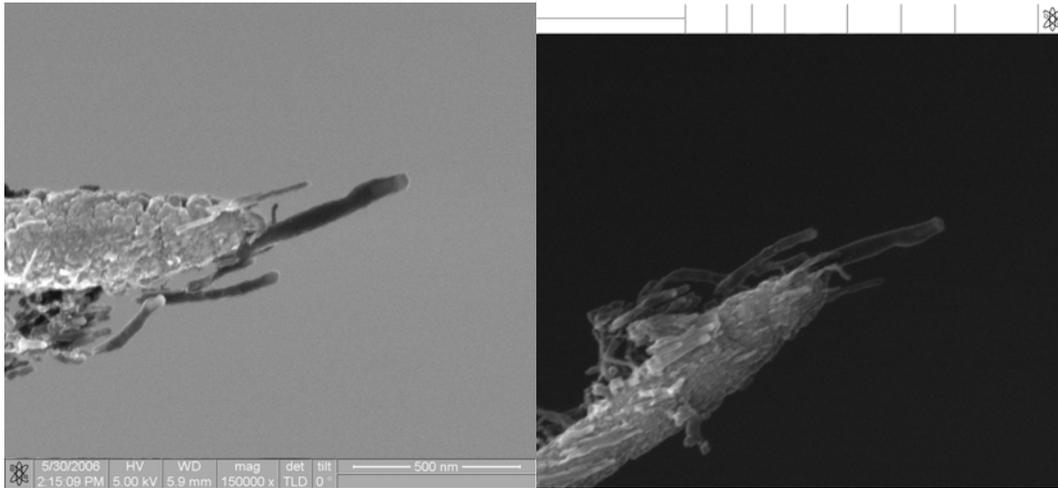


Figure 3.12: Left, a CNT on a tip before field emission experiments. Right, shows the same tip after a week of data was taken, unchanged; the tip has been rotated 90°. The next chapter will show examples of CNTs after four weeks of data.

3.13 SUMMARY

A new process has been developed to grow single CNTs on tungsten tips. The yield approaches 50% but could be improved further by better controlling the production parameters. CNTs grown have been observed to be consistently aligned along the primary axis and form a robust bond with the tungsten wire. This method is a major advance in CNT growth and brings the prospect of CNT electron sources much closer to market.

3.14 REFERENCES

- [1] Thesis K.B.K. Teo, Cambridge University, 2002.
- [2] N de Jonge, M Doytcheva, M Allieux, M Kaiser, S. A. M. Mentink, K. B. K. Teo, R. G. Lacerda, W. I. Milne; *Advanced Materials* 2005, 17, No 4, 451-4.
- [3] N. de Jonge, M. Allieux, M. Doytcheva, M. Kaiser, K.B.K. Teo, R.G. Lacerda and W.I. Milne. "Characterization of the field emission properties of individual thin carbon nanotubes", *Applied Physics Letters* 85, 1607 (2004).
- [4] K.B.K.Teo, S.-B. Lee, M. Chhowalla, V. Semet, Vu Thien Binh, O Groening, M. Castignolles, A. Loiseau, G. Pirio, P. Legagneux, D. Pribat, D.G. Hasko,

- H. Ahmed, G.A.J. Amaratunga and W.I. Milne. *Nanotechnology* 14 (2003) 204–211.
- [5] Aldo R. Boccaccinia, Johann Cho, Judith A. Roether, Boris J.C. Thomas, E. Jane Minay and Milo S.P. Shaffer. Electrophoretic deposition of carbon nanotubes. *Carbon*, Volume 44, Issue 15, December 2006, Pages 3149-3160.
- [6] Ovsyanko, Mikhail Mikhailovich (2006) Ion sculpting of Cu(001). Thesis. University of Twente, The Netherlands.
- [7] E. Minoux, O. Groening, K. B. K. Teo, S. H. Dalal, L. Gangloff, J-P Schnell, L. Hudanski, Ian Y. Y. Bu, . Vincent, P. Legagneux, G. A. J. Amaratunga, and W. I. Milne; *Nanoletters* 2005, Vol. 5, No. 11 2135-2138.