

2 ENGINEERING THE SYNTHESIS OF CARBON NANOTUBES

Contrary to popular belief, carbon nanotubes (CNTs) were not discovered by Iijima [1] in 1991, but by Radushkevich and Lukyanovich [2] in 1952, who published clear images of 50 nm diameter tubes made of carbon in the Russian Journal of Physical Chemistry. Unfortunately, scientists in the west did not have access to this journal because of the Cold War and together with the fact that the article was written in Russian, it went largely unnoticed.

Indeed, this is not the only article to go unnoticed. Carbon nanotubes have been produced and observed under a variety of conditions prior to 1991. In 1976 Oberlin et al [3] showed a TEM of single-walled, nanometre-sized carbon fibres produced by chemical vapour deposition. In 1981 a group of Ukrainian scientists characterized their structure and chemistry [4] and suggested the armchair and chiral structures of the graphene sheets with which we are familiar today.

Iijima discovered CNTs in the insoluble material of arc-burned graphite rods and went onto produce extensive work on arc-discharge grown CNTs. However, because Iijima's paper was published in Nature, it was only then that interest in devising growth methods and applications started in earnest, which demonstrates the importance of publishing new work in highly ranking journals.

2.1 CARBON NANOTUBE SYNTHESIS METHODS

The synthesis of CNTs is of the utmost importance if they are to be seriously considered for device applications. It is possible to choose from a range of synthesis methods but they each have their relative advantages and disadvantages. The lack of CNT-based products available in the marketplace indicates the level of difficulty engineers have to overcome in utilizing the various synthesis methods to produce stable, reliable CNT devices. This shall be discussed next.

2.1.1 SYNTHESIS OF CNTS BY ARC DISCHARGE

CNTs were observed in 1991 when Iijima was trying to grow C_{60} fullerenes [1]. The method used was the arc discharge method. Two carbon rods separated by approximately 1 mm are placed end to end in a chamber which is either at low pressure or filled with inert gas [5]. A direct current of 50-100 A driven by a potential difference of ~20 V creates a high temperature discharge between the two electrodes. The discharge partly vaporizes one of the carbon electrodes and forms a small, rod-shaped deposit on the other electrode. On analysing the contents of the rods, there is a large amount of amorphous carbon – as much as 70% [6]. To improve the yield, catalyst metals such as Ni, Fe or Co are added to the graphite rods [7] which results in catalyst particles being trapped inside the grown CNTs. Figure 2.1.1 illustrates both a schematic of typical apparatus used and the resultant CNTs grown.

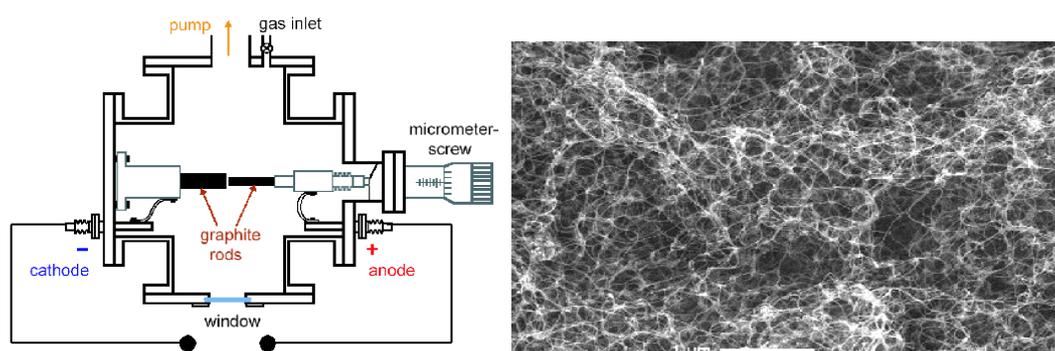


Figure 2.1.1: Left shows a schematic diagram of typical apparatus used to synthesize CNTs by the arc discharge method. Right, an electron micrograph of CNTs grown by this method. Note the disordered nature of the grown CNTs. The scale bar is 1 micron.

Arc discharge produces both single-walled and multi-walled CNTs of varying lengths. The CNTs are normally highly crystalline, have few defects and can be as long as 50 μm , but during synthesis they are covered by amorphous carbon detritus [8]. Consequently, CNTs grown by this method must be purified and separated before they can be put to significant use. A typical method [9] is to thermally anneal the CNTs in air at ~500 $^{\circ}\text{C}$, which burns away the carbonaceous detritus, followed by continual immersion and filtering in a strong acid, such as HCl, to remove the catalyst particles. To separate the CNTs, boiling in 30% nitric acid is a typical technique.

2.1.2 SYNTHESIS OF CNTS BY LASER ABLATION

Laser ablation works using similar principles to arc discharge, the difference being that with this method, a pulsed laser is focused onto a graphite target in a high temperature reactor. An inert gas is bled into the chamber and CNTs form on the cooler surfaces of the reactor when the vaporized carbon condenses. The process was invented by Guo et al [10]. Guo modified an existing process used to create metal molecules; he substituted the metal target for graphite. The method was later refined when the graphite targets were changed to a graphite-catalyst composite, the best yield coming from a 50:50 mixture of cobalt and nickel, to synthesize single-walled CNTs [11]. Figure 2.1.2 illustrates both a schematic of typical apparatus used and the resultant CNTs grown.

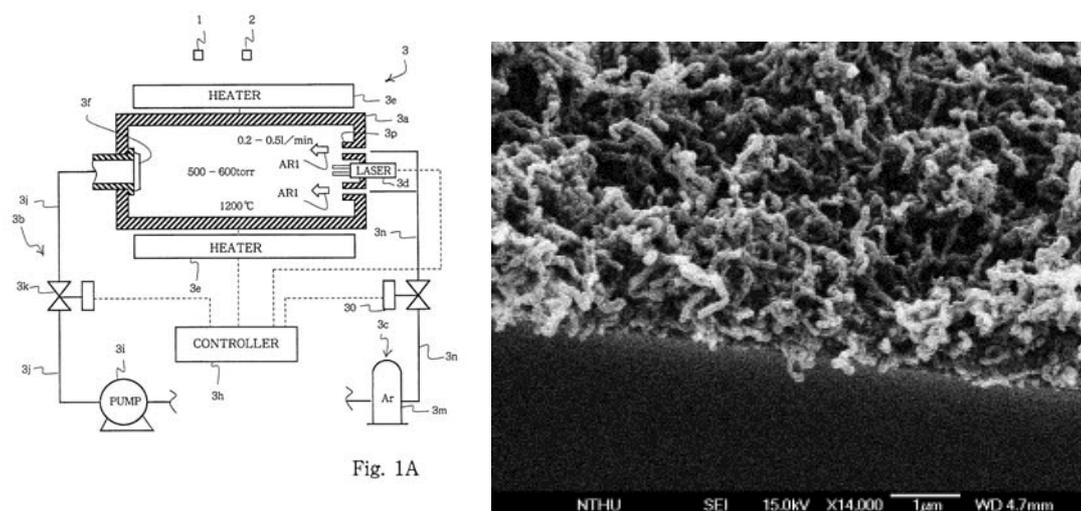


Figure 2.1.2: Left shows a schematic diagram of typical apparatus used to grow CNTs by laser ablation. Right, a typical result of CNTs grown by laser ablation. Note the lack of orientation in the grown CNTs. The scale bar is 1 micron.

Even though this method only produces 30% detritus – the same purification and separation procedures must be observed – it is the most expensive [6], widely used method. However, the diameter of the CNTs can be controlled by altering the reaction temperature which arc discharge cannot control.

Both arc discharge and laser ablation are the principal methods for synthesizing small quantities of high-quality, low-defect CNTs. However, both methods involve sublimating the carbon source, so the process isn't realistically scalable to mass

production. Also, these methods both produce tangled CNTs immersed in amorphous carbon detritus, so it is not practicable to make even small electrical devices with these CNTs due the great difficulty in manipulating single CNTs on the nanoscale.

2.1.3 SYNTHESIS OF CNTS BY BALL MILLING

On placing graphite powder into a stainless steel container along with hardened steel balls, the container is purged and argon introduced. The powder is milled continuously at room temperature for a week. After milling, the powder is annealed under inert gas flow at ~ 1400 °C for 6 hours, which produces CNTs [8].

This method produces more multi-walled CNTs than single-walled, but suffers from the same manipulation problems as arc discharge and laser ablation.

2.1.4 SYNTHESIS OF CNTS BY CHEMICAL VAPOUR DEPOSITION

The deposition of carbon from hydrocarbon vapour with the use of a catalyst was first reported in 1959 [12], but CNTs were not synthesized by the chemical vapour deposition method, or CVD method until 1993 [13]. The process is commonly enhanced by the addition of plasma (plasma-enhanced CVD, or PECVD) which can reduce the temperature required to initiate CNT growth and induces alignment of the grown CNTs because of the high local electric field.

The process involves two steps, the preparation of the catalyst on a surface and the growth by the decomposition of reactant gases.

2.1.4.1 FORMATION OF THE CATALYST FOR CHEMICAL VAPOUR DEPOSITION

The catalyst metals commonly used for nanotube growth are Fe, Ni and Co [14]. There are several routes to the production of catalyst nanoparticles, the three main methods being the wet catalyst method, etching of a catalyst metal and the coalescence of thin catalyst films.

The wet catalyst method involves the deposition of a metal nitrate/bicarbonate solution onto a surface. On drying, the salt in the solution crystallizes to form small islands of the metal salt. The salt is reduced to a metal oxide by heating or calcinations and the oxide is then reduced by H₂ and/or thermal decomposition resulting in the formation of metallic catalyst islands from which the CNTs grow [15, 31].

The etching technique involves depositing a layer (<100 nm) of the desired catalyst metal by either evaporation or by sputter coating. Catalyst islands are formed this time by bombarding the catalyst metal with ions or by plasma etching [17, 18].

The most commonly used form of catalyst preparation for devices is coalescence (shown in figure 2.1.4.1c).

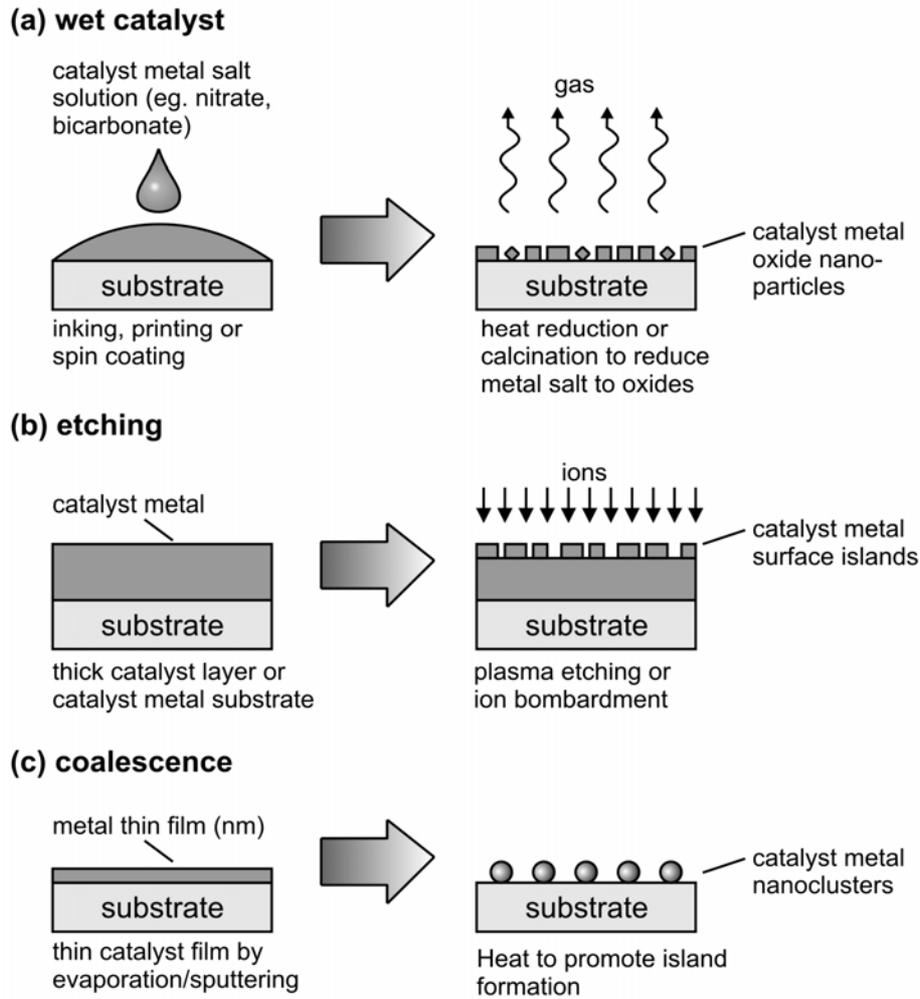


Figure 2.1.4.1: Methods of producing nano-sized catalysts for nanotube growth

A thin film (typically less than 10 nm) of Fe, Co or Ni is deposited onto a substrate by evaporation or sputter coating. Upon heating, the thin film breaks up (known as dewetting), agglomerating to form nanoislands as a result of increased surface mobility and the strong cohesive forces between the metal atoms [32, 33]. CNT growth then nucleates from these nanoislands.

2.1.4.2 GROWTH BY CVD AND PECVD

To initiate CNT growth, two gases are inlet into an evacuated reaction chamber, a process gas (such as ammonia, nitrogen or hydrogen etc) and a carbon-containing gas

(such as acetylene, ethylene, methane, ethanol etc) at a temperature of 550-900°C. Growth occurs at the site of the metal catalyst. The carbon-containing gas is broken down at the surface of the catalyst particle which then diffuses around or through the particle (dependent on conditions) to the edge of the particle where the CNTs form. The mechanism of this process is still controversial.

Catalyst particles stay either at the tips of the CNTs during the growth process or they stay at the base of the CNTs depending on the adhesion between the catalyst particle and the support (as shown in figure 2.1.4.2.1).

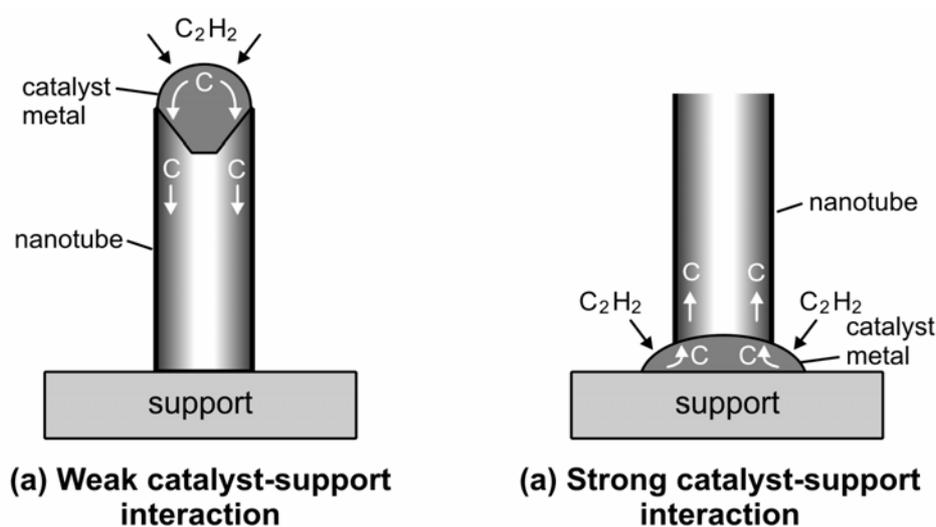


Figure 2.1.4.2.1: There are two types of growth, tip or base growth, which results from differences in the catalyst-support interaction [14].

In CVD, the energy required to break down the reactant deposition gases into graphene comes solely from the heat supplied to the catalyst particle and its immediate environs. There is no alignment of CNTs from the CVD process. The grown CNTs are often randomly orientated and resemble spaghetti. However, under certain reaction conditions, even in the absence of a plasma, closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a carpet or forest. In PECVD, the applied plasma creates a sheath above the substrate in which an electric field perpendicular to the substrate is induced. This field breaks

down some of the deposition gases and vertically aligns the CNTs as they follow the induced field. This is shown in figure 2.1.4.2.2.

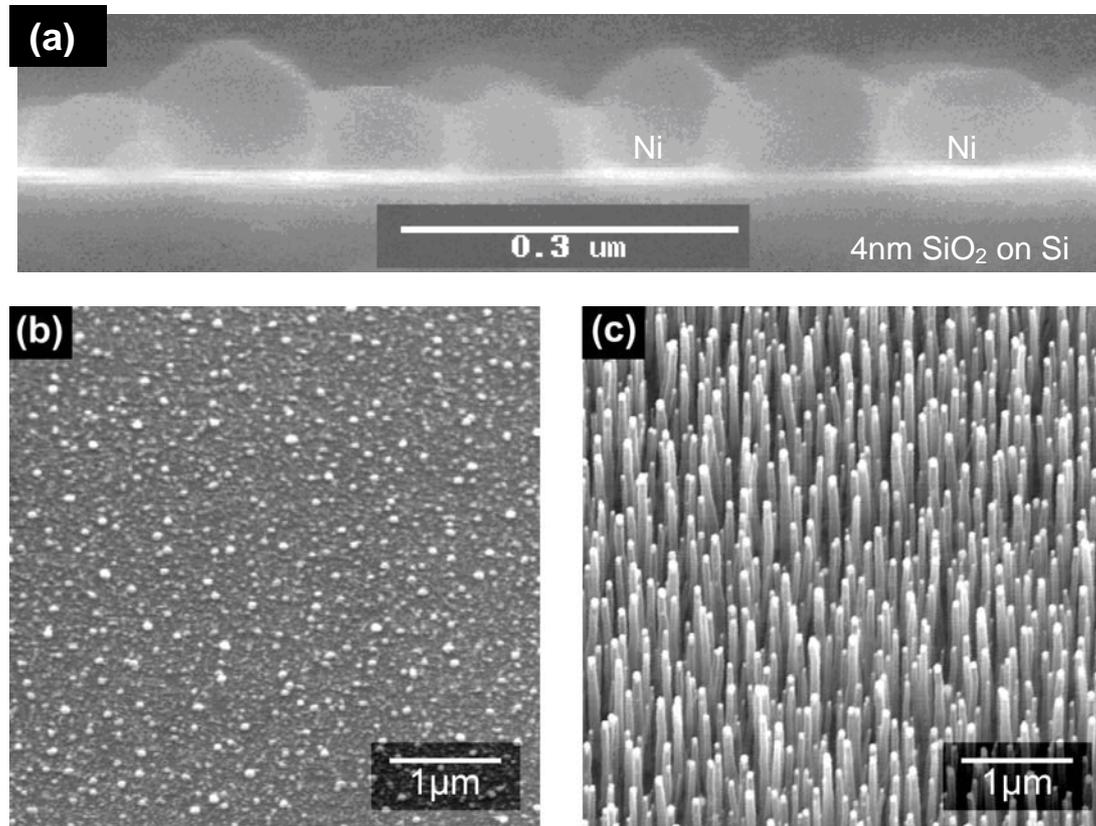


Figure 2.1.4.2.2: When Ni nanoclusters ((a) and (b)) are on a 4 nm layer of SiO₂ deposited onto a Si substrate, they exhibit weak interactions (c.f. ‘hydrophobic’) with their supports hence favouring tip growth (the Ni is the high contrast dot seen at the tip of the nanotube as in (c)).

Both CVD and PECVD hold a number of advantages over other synthesis methods. For tip growth, nanotube length increases with deposition pressure, and linearly with deposition time up to certain lengths [21]. The diameter is controlled by the thickness of the catalyst deposited and the position of the CNTs can be controlled by where the catalyst is positioned. For instance, lithographical techniques can be employed to deposit catalyst dots to control the position of grown CNTs which can be employed in field emission devices [22]. What this results in is much more control over the dimensions of the CNTs and removes the need to purify and separate CNTs grown by other methods.

2.2 GROWTH OF CNTS ON THREE-DIMENSIONAL SURFACES

The aim of this research was to produce a working field emission source with a CNT as the source of electrons. Current field emission sources consist of an etched tungsten hairpin, welded to a filament which is used to heat the device. This covered by an extractor. The etched tungsten source needs to be aligned on axis $\pm 5 \mu\text{m}$ and with the flat surface of the etched tungsten wire exactly 90° to the beam axis; otherwise image resolution will be compromised due to the effect of astigmatism.

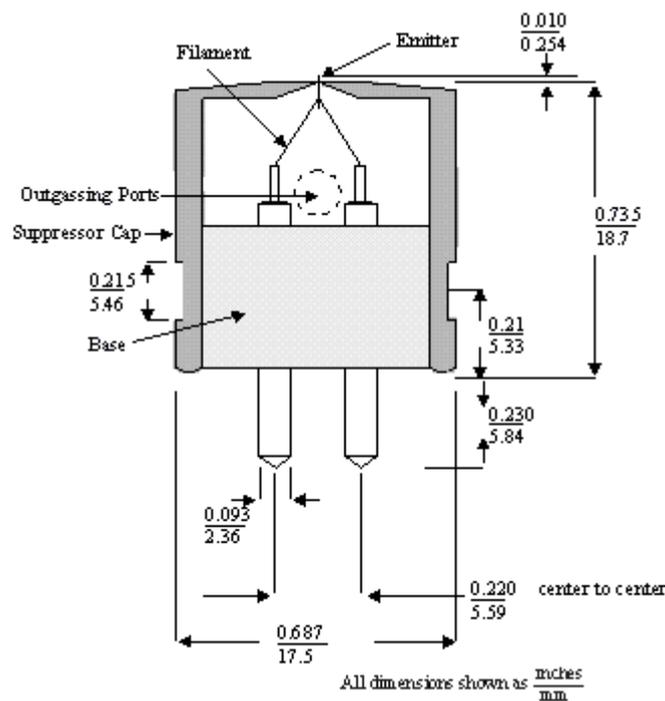


Figure 2.2.1: Schematic of a tip made at FEI in Oregon. The ceramic base holds two metal prongs, with a crosswire connecting the two. At the vertex of the crosswire, the tip is attached. This should be attached with the whole shaft of the tip centrally located on-axis so it can be aligned with the rest of the column. The suppressor (in dark grey) is also shown on this diagram. It is fixed to the ceramic base by grub screws under compression.

With all the electron beam equipment in use in the world using sources such as these, it makes sense to try to integrate the CNT into such a fixture. This, however, creates a

number of problems. Measurements made by de Jonge et al [23] were taken from CNTs attached by a “cut and stick” method described below.

A forest of carbon nanotubes grown by Teo et al [23] was placed in an electron microscope with a tungsten tip. Carbon glue was applied to the tungsten tip which was brought close to the carbon nanotubes (see Figure 2.2.2). On applying a potential difference between the tip and the carbon nanotube, one of the carbon nanotubes was attracted to the tungsten tip and will attach itself by sticking to the carbon glue. When the tip is withdrawn, the nanotube splits, resulting in a carbon nanotube attached to the side of the tip through which field emission measurements can be made.

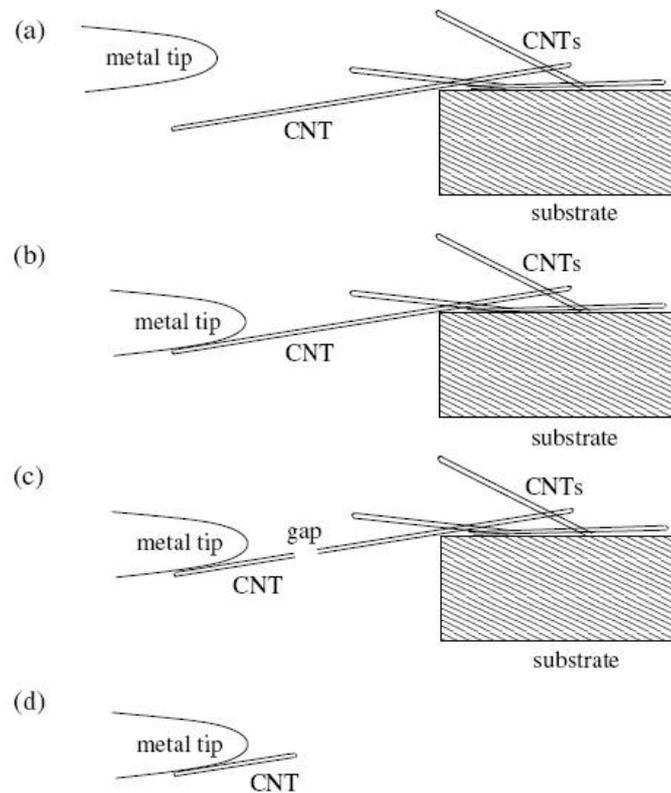


Figure 2.2.2: A schematic of the carbon nanotube attachment process. a) shows a metal tip approaching a forest of randomly arranged nanotubes, b) shows a nanotube attached to the metal tip, c) shows the withdrawn tip splitting the carbon nanotube, d) is the resultant tip which is used for measurement [23].

There are a number of drawbacks to this process. Although it is possible to select a CNT with a particular diameter, it is not possible to control its length. When the tip is withdrawn, the CNT snaps at a point of weakness. There is no way of telling where this point of weakness is, so the CNT that is attached to the end of the tip could be of any length. The CNT attaches to the side of the tip and is consequently off-axis. There is little control over CNT alignment, so when the CNT attaches it could well attach at any angle (see figure 2.2.3).

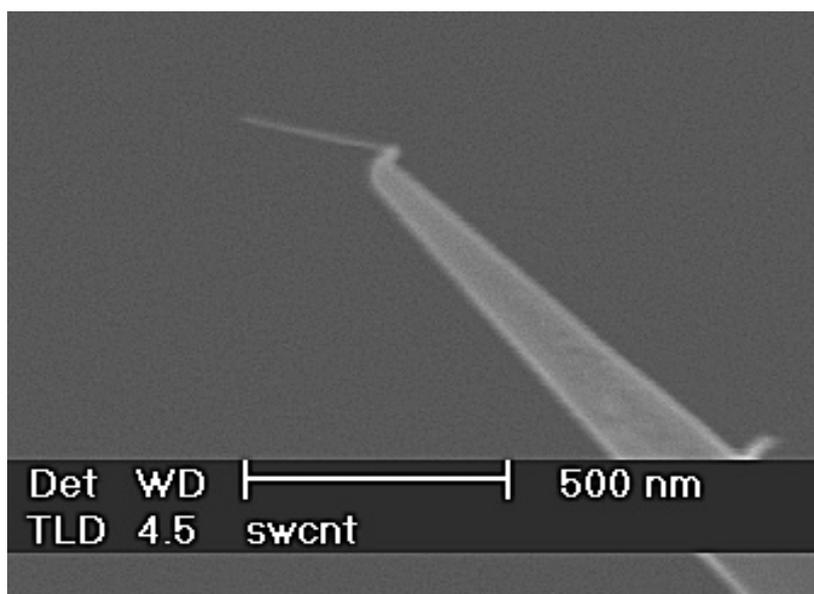


Figure 2.2.3: Electron micrograph showing the large angle at which a CNT is often attached to a tip by this process.

It is not clear what the bond between the tungsten tip and the CNT is. In the author's experience, transportation across large distances is enough for the CNT to fall off of the tip. This indicates that the bond between the CNT and the tip is weak and one would imagine that the lifetime of such a tip would be quite poor due to this weakness. Finally, the process of attaching a tip can be extremely time-consuming and awkward. The author attempted this process and took 45 minutes to attach a tip using this method in de Jonge's laboratory. An experienced user, Erwin Heeres, took 20 mins to attach the CNT shown in figure 2.2.4.

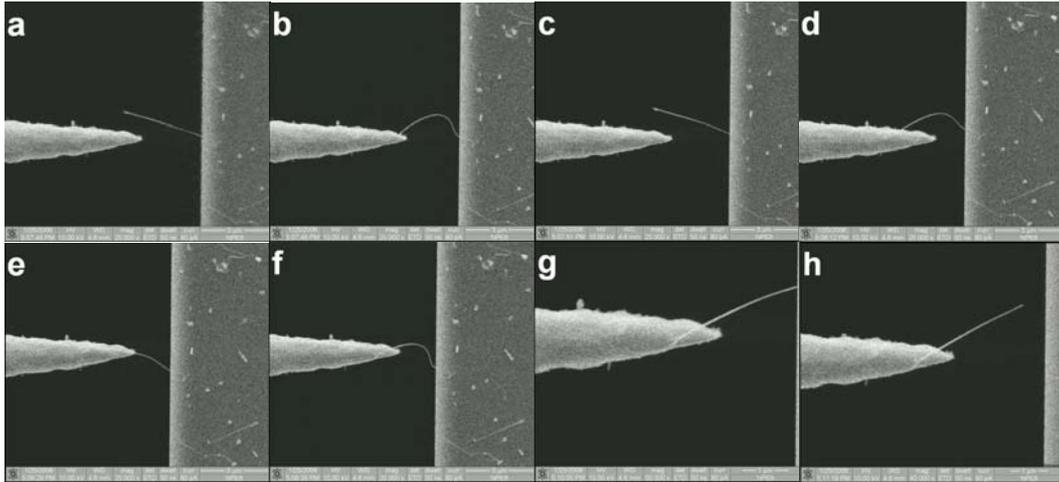


Figure 2.2.4: Sequence of electron micrographs showing the attachment process of a CNT tip by Erwin Heeres at various magnifications. The tip apex radius is approximately 100 nm. In (a), the CNT is brought close to the tip. In (b), a potential difference is applied between the CNT and the tip and the CNT attaches, but only partially, as the contact is lost at (c). In (d) the tip has been moved closer to the CNT and a potential applied again. The tip is moved in (e) showing a stronger bond this time. In (f), attempts are being made to snap the CNT; it breaks by (g). (h) shows the resultant tip attached at about 30° off-axis.

From figure 2.2.4 it is safe to conclude that the scaling up of this process to mass production is impractical and that an alternative fabrication process needs to be found if CNT electron sources are to be realised.

One possible solution is to use a silicon chip with a single CNT in the centre, which has been grown after the catalyst is positioned by lithographical means. However, it is important to emphasise that this creates a huge amount of difficulty in the mounting of the silicon chip in existing columns and would create a great deal of undesired expense for electron beam manufacturers to modify their systems to accommodate such an electron source. The following suggested solution illustrates the difficulties involved.

2.3 POSITIONING OF A SINGLE CNT IN THE CENTRE OF SILICON CHIP

An idea mooted by the sponsors of this PhD, FEI Company, involves the use of a Vogel mount, a mount which is used to hold a LaB₆ emission source (shown in figure 2.3.1)

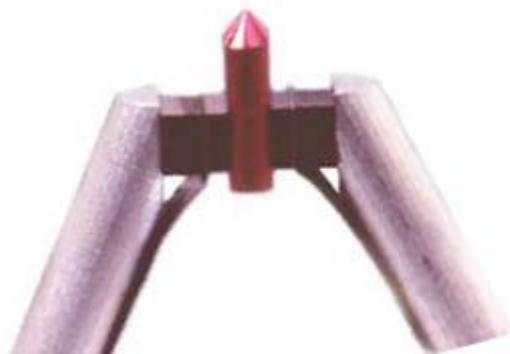


Figure 2.3.1: A typical LaB₆ electron source. The LaB₆ is the purple crystal in the centre and is supported under compression by graphite.

The mount consists of two arms which act as a spring. The LaB₆ emitter is placed in the centre of this together with structure and is supported by two graphite pads on either side. Current is passed through the structure to heat the tip.

The idea proposed involved replacing the LaB₆ with a silicon chip with one carbon nanotube in the centre. The author attempted this but found a number of problems, some insurmountable.

A silicon chip 300 μm thick and approximately 20 \times 20 mm was scored on its rough surface along the crystal planes to approximately half its depth to leave 1 \times 1 mm squares (see figure 2.3.2a). The silicon chip was reversed, spin-coated in PMMA resist, dried and an array of dots exposed by e-beam. The dots were developed and lifted off; the silicon chip was sputter coated in 15 nm ITO followed by 7 nm Ni, followed by a lift-off of the rest of the PMMA to leave catalyst dots on the silicon chip defined by the size of the exposed array. Initially, a spacing of 8 μm was decided upon to maximize current density from 2 μm high CNTs on a chip placed in a Vogel

mount (see figure 2.3.2b). Work by Groening [26], Nilsson [27] and Bonard [28] state that the best current density is achieved when the CNTs are separated by twice their height, when field shielding is taken into account. However, as turn-on voltage was a key concern, due to the unfavourable geometry, and from simulations carried out by the author, CNTs separated by four times their height still provide a significant current density whilst almost completely removing field shielding between adjacent CNTs.

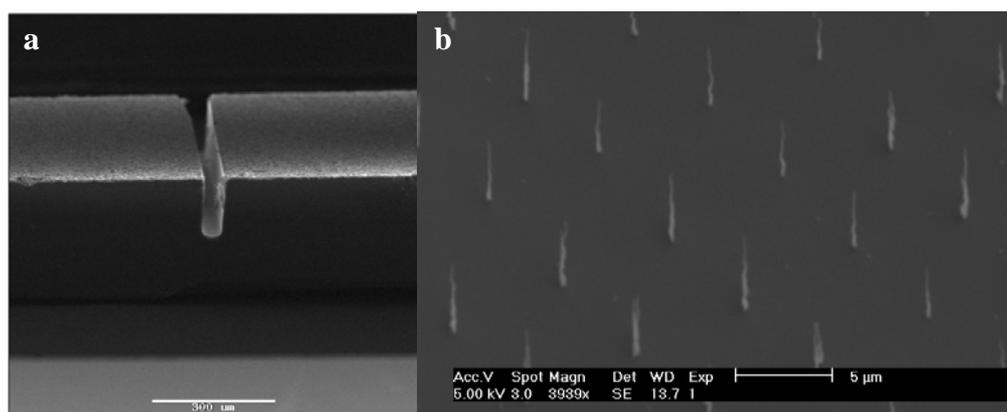


Figure 2.3.2: (a) shows a silicon chip scored to a depth of 150 μm . (b) shows an array of CNTs grown on to the silicon chips with a separation of roughly twice their height. The angle of inclination is 22° .

CNTs were grown to a height of 2-3 μm on a silicon chip. The chip was then split along the lines scored on its back. This in itself created a great amount of difficulty as the score lines were on the bottom (necessitated for lithography as PMMA does not distribute evenly on non-uniform surfaces) and the CNTs on the top. The chip could not be flipped upside-down because this would have destroyed the CNTs. It was still possible to break them up but with a great loss of CNTs. Of the chips that did survive the cutting process, edges would be very jagged. This is completely undesirable, as the sprung legs on the Vogel mount would simply snap out anything placed between them whose surface was not flat enough. This necessitated grinding of the edges of the chips so that they could be used in the Vogel mount. This created problems because the chips were difficult to hold (because they were so small and jagged) and because a large amount of dust would come from this process, sometimes completely coating the small chip. Having started with eighty 1×1 mm chips, five survived this processing. Finally, mounting the chips in the Vogel mount was also difficult. Due to

their small size and shape, positioning the chip in the mounting apparatus created difficulties; it was almost impossible to get the chip to line up. The resultant source that was eventually fabricated was angled about 10° to the horizontal. The chip was also significantly below the top of the graphite pads holding it in the mount. This was necessary because chips placed at the top of the mount sprung out once the arms were released. The position of the chip will have resulted in a further reduction in field enhancement. Even so, this was considered acceptable enough for a proof of concept device. The other 4 chips were lost during the mounting process.

Upon installation in a vacuum chamber for field emission measurements, it was found that the turn-on field for the CNTs on the chip was 9×10^5 V/m. As there were so many CNT emitters, the current was stable, but significant emission was detected up to 80° off axis on an adjacent phosphor screen.

Nevertheless, attempts were made to grow single CNTs in the centre of silicon chips using this process. Unfortunately, it was very difficult to grow just one CNT over such a large area (see figure 2.3.3). Impurities and bubbles in the PMMA or inadequate lift-off could all have contributed to the failure to grow just a single CNT in the middle of the chip.

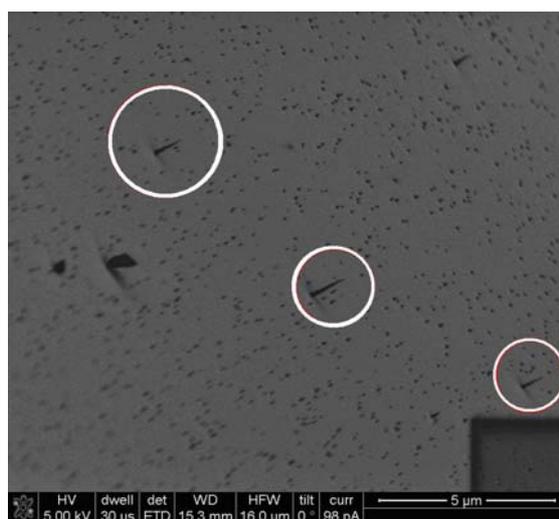


Figure 2.3.3: The white rings highlight additional CNTs that have grown on the Si chip despite there being one catalyst dot on the entire Si chip.

Another method suggested was to use pyramids employing a similar method to that used by Bell [29]. With this method, Bell produces an array of pyramids etched into silicon adjacent to each other as shown in figure 2.3.4. He then floods the gap with PMMA until the PMMA reaches the top of the pyramids. This provides a flat surface through which lithography processing can be carried out. However, a single CNT on a chip and thus a single pyramid is required for application to electron beam emission sources and this process cannot be applied as there are no adjacent pyramids with which to hold the PMMA in place. PMMA spin-coated onto an uneven surface results in uneven coating which prevents the use of lithography. Another point is that in order to focus the e-beam onto an object of the required height, another object of the same height is required in the immediate vicinity. Anything used to focus an electron beam will expose PMMA and will consequently be developed, which will result in a CNT grown where the beam was focused as well as where originally desired. This would again result in an undesirable multi-source.

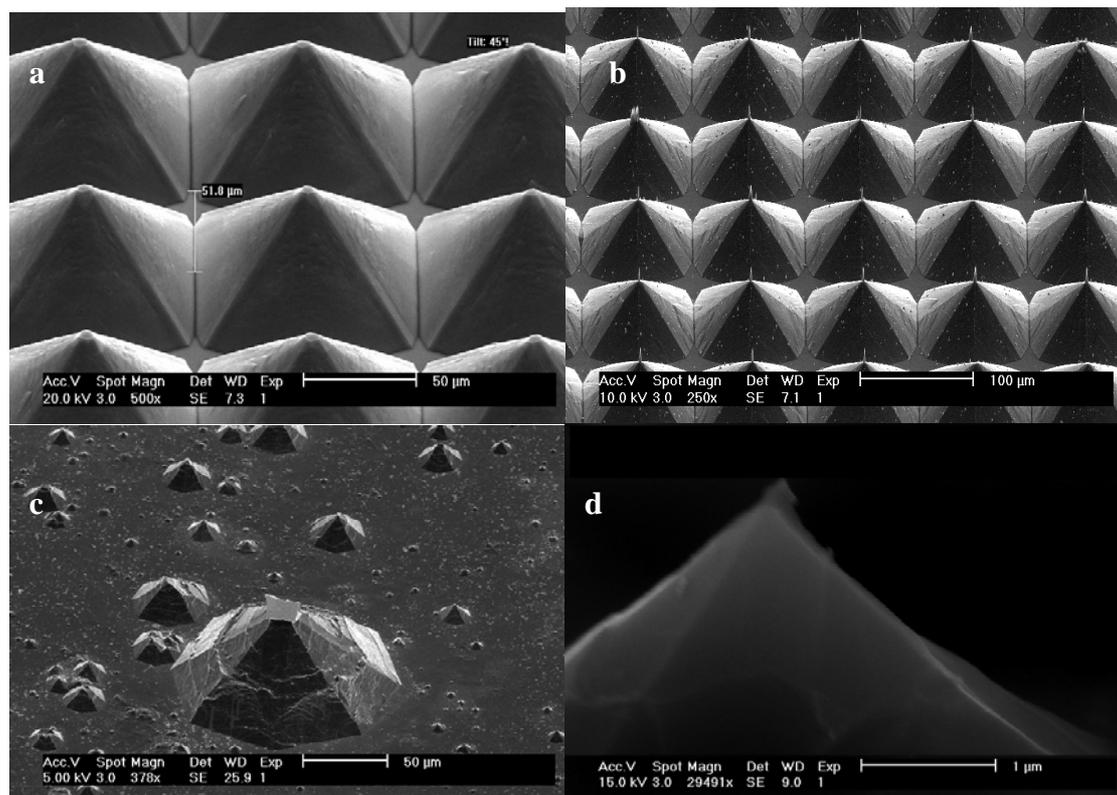


Figure 2.3.4: (a) shows pyramids etched by Bell, (b) shows CNTs on pyramids grown by Bell, (c) shows a single pyramid etched in the middle of a 1×1 mm Si chip, (d) illustrates the difficulty in forming a uniform layer of PMMA on the Si pyramid. The

PMMA can be seen in the form of a spike at the top of the pyramid with a much larger deposit towards the bottom on the right-hand side.

Other proof-of-concept devices were fabricated for use in a proposed microcolumn currently being developed by Philips Research Laboratories, Eindhoven, The Netherlands. The idea was to address a CNT positioned in the centre of a Si chip with a small microextractor (see figure 2.3.5). There would be other CNTs on the chip. A pattern consisting of four arrows points to the position of the CNT on the chip. From the arrows, CNTs would grow, but because these CNTs are so close together, their field enhancement is vastly reduced with no current coming from them when the central CNT operates. The design reduced the number of lithography steps required.

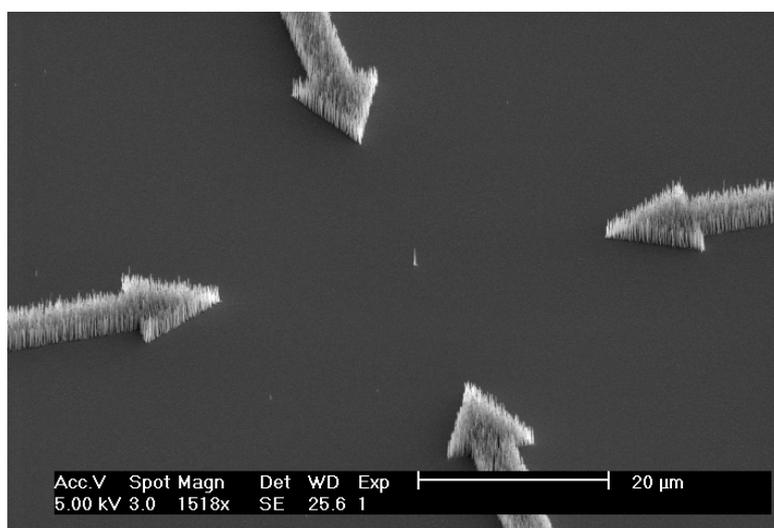


Figure 2.3.5: A single CNT observed in the centre of a Si chip with CNT forests in the shape of arrows pointing towards the central CNT.

However, the same problem of single CNTs growing elsewhere combined with field emission still coming from the arrows results in an undesirable high leakage current which is much higher than the current coming through the extractor itself.

From this work it has become apparent that single silicon-based CNT sources are very difficult to fabricate. Whilst there may be a solution to many of the problems identified, the cost of integration into existing electron beam machine designs would be enough to deter manufacturers with modest-sized research and development budgets from integrating CNTs into their system. Since testing equipment is also

based around the tungsten wire electron source, it was deemed better to persist with this design to enable the advancement of CNT electron source technology.

2.4 DIRECT GROWTH OF CARBON NANOTUBES ONTO THREE-DIMENSIONAL SURFACES.

Growth of CNTs onto metal tips in itself presents a significant challenge. The reason for this is threefold. The very fact that it is three-dimensional prevents the use of electron beam lithography; the electron beam cannot be focused onto the tip. One CNT is required at the apex because electrons should come from only one source. The CNT needs to be positioned in the centre of the tip and must be aligned along the axis of the tip to reduce the effects of astigmatism. Work in the next few paragraphs was undertaken in 2002 as part of research work for the author's undergraduate degree and is included for the sake of completeness.

Work was carried out to investigate whether the CNT could be used to ionize gas by field ionization, particularly helium (which has the highest ionization energy of 2372 kJ/mol, the highest of all elements) for use in a helium beam microscope [30]. The field required to ionize gas is typically ten times that required for field emission, typically a few volts per angstrom. An agar filament was coated in iron nitrate solution and allowed to dry. It was then placed into a reaction chamber with a current supply to heat the filament and a gas pipe to supply reactant gases. After evacuation of the chamber, NH_3 gas was inlet 100 sccm to reduce and remove the nitrate leaving iron particles to act as a catalyst; then the filament was heated to 700 °C followed by the inletting of C_2H_2 gas 25 sccm for 15 minutes. The result was a bundle of CNTs grown from some of the iron particles on the surface, as shown in figure 2.4.1.

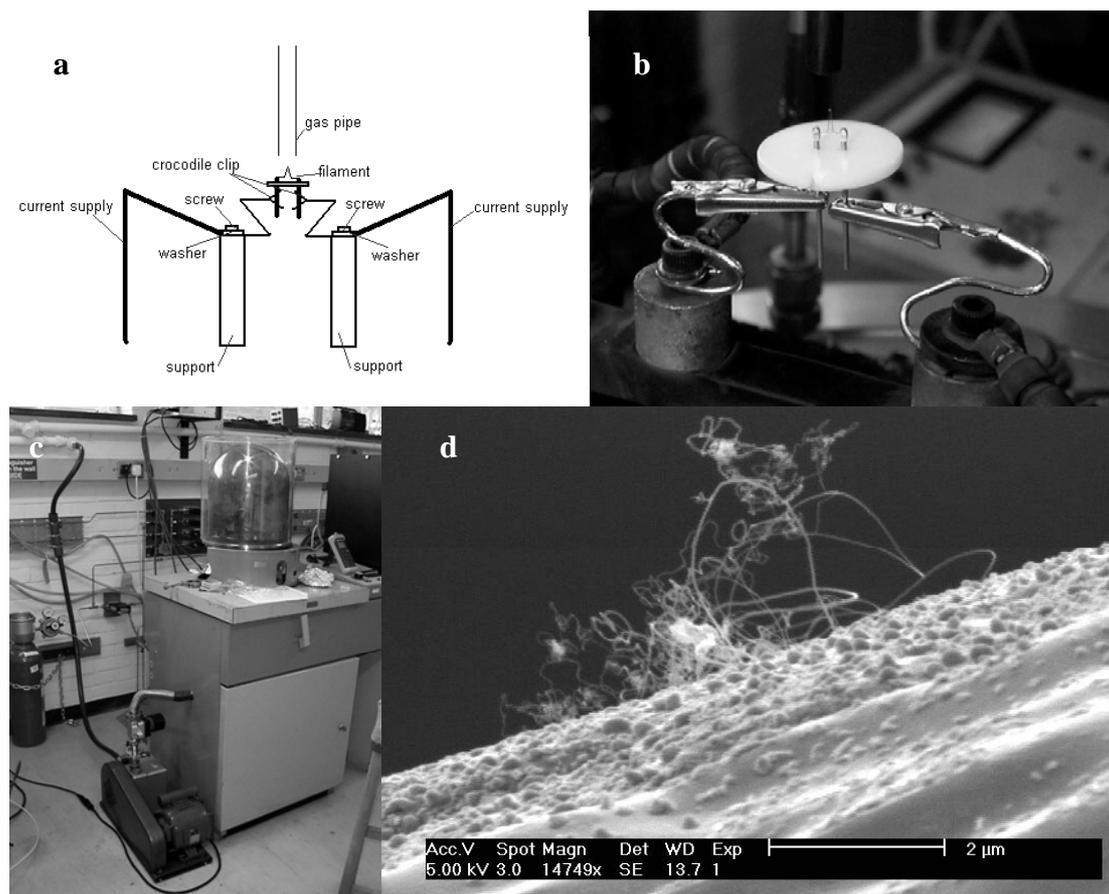


Figure 2.4.1: (a) shows a schematic diagram of the filament setup in the bell jar, (b) shows the filament inside the bell jar, (c) shows the machine used to grow the CNTs and (d) shows the result of CNTs grown on filaments. Spaghetti-like CNTs can be seen in the background, unactivated catalyst particles can be seen in the foreground.

Next, stainless steel wire was etched in orthophosphoric acid to a radius of a few hundred nanometres. The etching process was not easily controlled, so there was a range of radii. The steel was considered to be a catalyst itself, as the iron contained within could nucleate CNT growth. The wire was welded to a tungsten wire filament and placed inside the same reaction chamber. CNTs indeed grew, but because they were highly defective, they broke upon the application of high electric fields (as shown in figure 2.4.2).

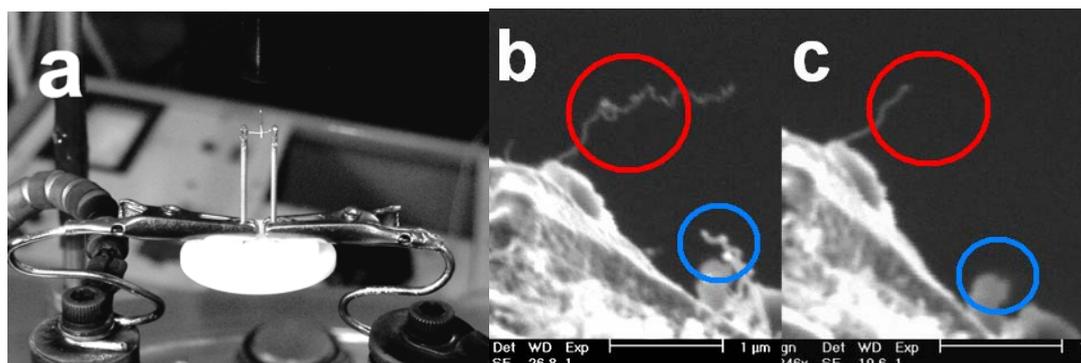


Figure 2.4.2: (a) shows the stainless steel wire welded to the tungsten filament in the reaction chamber. (b) shows CNT growth on the etched stainless steel tip; note its roughness. (c) shows the same tip but after field emission experiments. Comparing the red and blue rings in (b) and (c) shows how the defective CNTs have altered or disappeared as a result of the high fields the CNTs have been subjected to. It indicates the importance of producing high quality CNTs for reliable electron devices.

The next stage involved roughening the surface of the stainless steel tip after etching by reversing the bias in the etching process. A 10 second pulse was sufficient to roughen the surface at the apex. After growth, the resultant tip contained a dense forest of CNTs. The occasional CNT was longer, poking above the rest of the CNTs in the forest (see figure 2.4.3a). There were many of them. This tip was able to withstand the field required to ionize argon, with a first ionization energy of 1520 kJ/mol.

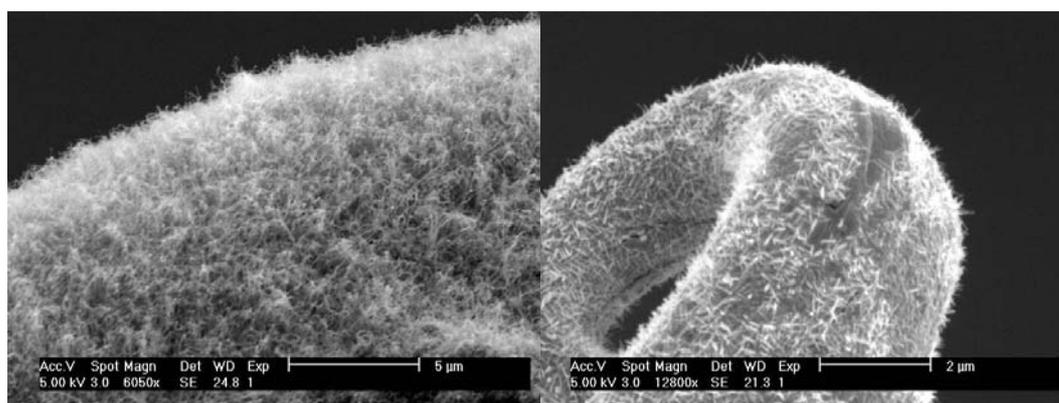


Figure 2.4.3: (a) shows a dense forest of CNTs grown on a large-radius steel tip. Some CNTs can be seen above the average height of the forest. (b) shows a tip with CNTs grown from Ni deposited by electroplating. The electroplating process caused the tips to deform.

Finally, an etched tungsten tip was electroplated with Ni. Unfortunately, the electroplating process damaged the tip, causing it to twist and contort. CNTs grew on the tip, but the field enhancement on them was reduced enough by the blunting of the tip to prevent ionization.

Following the undergraduate research project, further work was carried out on the forested tips. On increasing the voltage further, helium was indeed ionized whilst the tip remained largely intact (see figure 2.4.4). This suggests that CNTs are good candidates for stable field emission devices, as they can withstand fields ten times the minimum required for field emission.

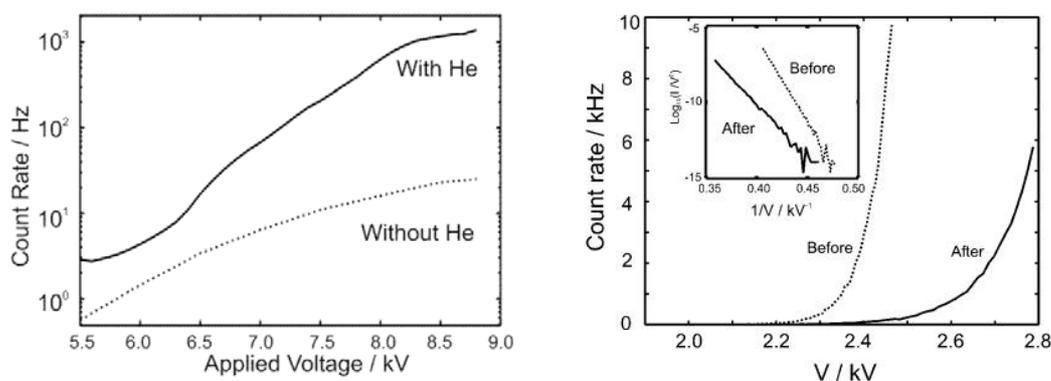


Figure 2.4.4: Left shows field ionization of helium from carbon nanotubes. The upper trace indicates the time-averaged detection current as a function of voltage applied to the CNT-coated wire. The dotted line indicates the “background” ion current, measured in the absence of admitted helium. Right shows field emission characteristics of the nanotube-coated steel wire before and after field ionization trials and (inset) the same data in a Fowler-Nordheim plot [31].

Despite the success of the helium project, the beam required from a CNT needs to be of a much higher quality. Plasma needs to be applied to the tip to induce alignment and to straighten the tubes and only one CNT can provide the electrons for the source, so only one CNT should be at the apex of the tip. Also, stainless steel tips were found to melt at relatively low temperatures. Consequently, tungsten with its high melting point offers a more durable base for CNT growth. CNT catalysis would have to come by other means. Work by this author with de Jonge, involved trying to deposit Ni onto

tungsten wire by pulsed electroplating. Unfortunately surface tension prevented Ni from being deposited only at the tip. Because of surface tension, the tip would be enveloped by the nickel solution. This resulted in Ni deposition a few tens of nanometres thick. There are also issues regarding the use of plasma to align the CNTs. Plasma breaks down to sharp objects in the same way that lightning hits trees and radio masts. Any sharp object protruding into a plasma will be hit by a burst of electrons which can destroy the tip and/or any chemistry that might be occurring there; certainly any growing CNTs.

2.5 SUMMARY

This chapter investigated various fabrication possibilities for carbon nanotube electron sources. It identified that PECVD offers the best route to controlling the dimensions and positions of multiple CNTs. However, electron sources require a single source of electrons and, therefore, a single CNT. This creates processing problems. Employing lithography causes problems because any beam applied needs to be focused before writing the dot from which the single CNT will grow. Any area used for focusing will also result in the growth on CNTs. Aligned growth on metal tips caused problems as well, because the application of plasma caused arcing to the tip.

The next section will address how these problems were addressed and will describe to how to grow one CNT at the apex of tungsten tips to make a reliable, high quality electron source.

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