6 DISCUSSION, CONCLUSIONS AND PROPOSED FUTURE WORK

It was clear at the beginning of this work that if the CNT cathode were ever to be realised, then a reliable, efficient fabrication process needed to be developed. Though the data collected by De Jonge et al. [1] gave very promising results, the method with which he attached CNTs to tungsten tips gave poor reliability, a huge amount of time wasted and a device that cannot be transported across large distances.

6.1 SILICON-BASED CNT SOURCES

Many avenues were explored; silicon was seriously considered as a support for the CNT, but there are quite significant problems with this approach that would need to be addressed. One of the most important aspects of the fabrication is that it must be a process from which *one* CNT results. Emission from multiple CNTs will cause interference and a very large energy spread. The most common method used to grow isolated CNTs is by electron beam lithography. Unfortunately, one needs to focus the beam first. Where the beam exposes, the resist develops resulting in CNTs also growing here. If the CNTs are positioned on a flat surface, upon the application of a voltage, these CNTs will also emit.

Work by Martin Bell at Cambridge [2] described the growth of individual CNTs on top of etched silicon pyramids, but the process resulted in a CNT growing on top of each pyramid. A potential solution to this would be to only expose one pyramid and to deposit a temporary marker on top of the resist in between pyramids. This can then also be used for focusing, and when the resist is removed, the marker is removed as well. This could mean that one could expose the top of a single pyramid, grow the CNT from that and place the chip in a Vogel mount.

However, there are problems with the Vogel mount. The edge of the silicon chip is almost always rough, so it is very difficult to align it perfectly horizontally. This also creates a problem for heating. Each tip-Vogel mount combination will have a significantly different resistance, so there will be no uniformity between cathodes. If silicon is to be pursued realistically as the base for the CNT, then a new tip-mount

combination needs to be designed and fabricated. It should not lose alignment when heated and the heating should be able to be controlled to high precision. This would require significant effort and it would also require modification to microscopes to accommodate such a design. This would not be desirable from an industrial point of view.

6.2 TUNGSTEN-BASED CNT SOURCES

There were many reasons for using tungsten over other metals as a base on which to grow CNTs in this work. The first was that the vast majority of electron sources are tungsten based anyway. There is a reason for this: tungsten can be etched easily with relatively innocuous NaOH or KOH solutions. Other metals require substantially more hazardous solutions e.g. orthophosphoric acid in the case of iron. The second reason was that it allowed for a "push-fit" electron source. The CNT sources were identical in appearance to Schottkys because they were grown in the same electron source module. The only difference is the nanoscopic CNT on the top of the tungsten tip. Thirdly, because of the knowledge base, etching of tungsten could be controlled to a very high degree and it was possible to etch ultra-sharp tungsten tips which became crucial to this project. Finally, one can obtain a very high field enhancement from a CNT on tip structure. The voltages required for extraction were more than an order of a magnitude smaller for the tip structure compared to the flat, silicon-based emitter.

PECVD is now a well-established process for the controlled, aligned growth of CNTs. This work modified the growth conditions so that aligned CNT growth was carried out on a high aspect ratio, 3D substrate for the first time. Ni was found to be the better catalyst with the recipes used, though Fe can be used to grow CNTs at a lower temperature if required. It was again very difficult to use lithography to deposit a single CNT at the top of the tip because the electron beam cannot be focused at the tip. It was also difficult to focus an ion beam at the apex.

Because of the knowledge base for tungsten wire etching, it was possible to etch the tungsten to radii of 50 nm and below. Because this is so small, it was possible to control the amount of catalyst deposited at the apex so that upon dewetting it could

form into a single catalyst ball. This method also has the advantage of using polycrystalline tungsten wire as the base, rather than the very expensive single-crystal tungsten.

There are, however, certain problems that need to be resolved. The single CNT yield is only 50%, which would need to be improved if CNT sources are to be sold commercially. Because the wire is polycrystalline, the microstructure of each tip will be different and it can be sometimes more favourable to have two catalyst particles rather than one at the top. A single crystal tungsten tip could be used, but the yield might also depend on the crystal orientation, so an investigation of this needs to take place. Unfortunately this would be quite expensive. The simulation results have shown that secondary CNTs must be comparable in height to the top-most CNT in order to effect field emission. Little control of the CNT length was achieved, though there was a reasonable control of the diameter to give a standard deviation of 20%. The prototype stage, which was patented, was a little crude for the precision required to hold these tungsten wires in a repeatable manner. The height at which the tungsten tip sits above or below the stage will have a great effect on growth rate because there may be a large difference in temperature and gas feedstock supply, and there may be a plasma etching effect whilst the CNT is growing. A high precision stage could decrease the variation in CNT height. A more precise stage would probably improve the alignment accuracy as well.

Rapid thermal annealing has been shown to improve the structure of the cap from which the emission current emanates. The process was modified to accommodate both hairpins and entire electron source modules. The latter is very exciting, since it is the first time that CNTs have been grown in situ on a device and that the addition of CNTs has been shown to improve the device’s performance.

The fabrication processes developed in this work could open up a whole new avenue of research. The principles used in manipulating the plasma in order to enable to the aligned growth of CNTs can be extended to other 3D objects. For instance, CNTs could be used as AFM tips, STM tips and biological probes. These are areas of particular interest for future work.

The CNT source does have some minor limitations. The first is that they decompose at temperatures ≥1300 ºC. Great care must also be taken in transporting the tips. They must always be stored in metal boxes to prevent electrostatic discharge. Great care must also be taken whilst installing the CNT into a microscope.

6.3 ELECTRON-OPTICAL PROPERTIES OF CNTS

It has been the tendency in the literature to exaggerate the electron-optical performance of CNTs. Whilst the numbers quoted for energy spread, for instance, were very low, they were taken at total currents so small that they could not possibly be used for any microscopy application. It was the author's intention to give a sober evaluation of the CNT's emission properties and to compare it properly with other electron sources.

It is important to complete the cap structure before field emission experimentation. Without this, the CNT will disintegrate once a moderate current is drawn from it. The cap structure is also required to increase stability.

The first few hours of field emission are very unstable, and it can take as much as a week for the emission to settle down. This is probably because of the gases adsorbed onto the CNT and tungsten tip during the fabrication process outgassing into the vacuum chamber. The problem is potentially greater for CNTs grown within electron source modules, since the surface area of the module is substantially larger. There are two possible solutions to this; either industry accepts this and sets up a rig in which CNT sources can be operated for a week until their instability decreases, or a new process is developed to clean the CNT sources after growth.

Stability is poorly defined in the literature. In this work, the author defined *instability* and *drift*. It would be ideal if an industrial standard is adopted so that sources can be properly compared. The author proposes such a standard as part of this thesis. One key aspect of the stability analysis was that *instability* (based on standard deviation)

and *drift* (based on maxima and minima) were found to be proportional to each other, with *instability* typically 20-25% of the value of *drift*.

This work has found that the CNT should ideally operate at lower total currents, typically less than 1 μA, since instability increases to beyond 1% above this value. This would be considered to be a disadvantage were it not for the fact that the CNT is significantly brighter than a Schottky source (3-10 times brighter) which means that much less total current is required for a similar signal. Instability has, at times, been found to be as low as a Schottky emitter, the best emitter for stability currently on the market.

Current feedback loops would offer a way of rectifying the step-like structure observed in the current. A simple program could do this.

Low pressure is required to operate CNT sources. At pressures above 5×10^{-9} mBar, instability increases by at least half an order of magnitude. This is probably down to surface contaminants having a significantly higher effect on the CNT at higher pressures because their concentration is higher. A possible mechanism is that a molecule comes close to the CNT and provides an alternative quantum mechanical path for the electron to go into vacuum. It may act to increase or even decrease the workfunction thus causing a fluctuation in the current. An investigation of various gaseous species leaked into high vacuum could be used to test this hypothesis and is another possible source of further work.

The kinetic energy spread measured is in agreement with the values quoted by De Jonge et al [3] because at higher currents he also found the energy spread to be 0.28 eV. Low energy spread values were obtained at currents lower than that used for e-beam equipment. It is clear that the energy spread is significantly better than a Schottky emitter and is at least as good as a tungsten cold-field emitter, the best on the market for low energy spreads.

6.4 MICROSCOPE OPERATION

Although this work is not the first to show a scanning electron micrograph with a CNT cathode, it is the first to show a micrograph of a viable CNT prototype cathode which can be reliably fabricated and scaled up to mass-production. The CNT source was found to take a long time to stabilize. This is probably a result of the increased adsorbant species accumulated during the fabrication process compared with a short tungsten wire.

Despite the stability problems, the initial measurements are very promising, exhibiting a higher resolution than a Schottky with identical column geometry and a much higher brightness, potentially 10 times as bright as a Schottky. A simple ballast resistor may improve stability also.

6.5 FUTURE WORK

The priorities are to find a way of controlling the height of the CNT with greater precision. An investigation should be made into whether single crystal tungsten would make a better base for more repeatable CNT growth and to improve the yield of single CNT tips. Lifetime tests need to be carried out and a way must be found of aligning one of the bright spots in the emission pattern onto the optical axis.

In the longer term, both theoretical and experimental investigations should be made into the nature of instability. Investigations should be made into the various mechanisms (electromigration, ion bombardment, surface adsorption and desorption) and to observe which gases have the most effect on the stability.

6.6 SUMMARY

This thesis shows that the CNT cathode works and though certain improvements could be made to the fabrication process, a large advance has been made in finally bringing a CNT device closer to market. The properties measured show that the CNT

source compares favourably with and in some cases improves upon other sources available today. Greater resolution and performance in microscopy will benefit the scientific community as a whole because it will open up the nanoscale to the community at large, whereas previously, only a select few would have been able to afford the machinery for nanoscopic surface research.

6.7 REFERENCES

[1] N. de Jonge, M. Allioux, 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**, (2004).

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