

6.1: Invited Paper: Design of Carbon Nanotubes for Field Emission Applications

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Abstract

Field emission from CNTs can be applied to many technologies because of their high current carrying capability, chemical inertness, physical strength and high aspect ratio. Depending upon their applications it can be more advantageous to use either individual tubes or arrays of tubes. Multiwall tubes or single wall tubes can also be utilised and in some instances aligned tubes are also necessary to provide the field emission currents required. This paper will present work on the optimisation of Carbon Nanotubes for applications including, field emission displays, electron microscopes, x-rays, and microwave sources.

1 Introduction

Various applications for CNTs in the ICT field have been touted but in the near term only a few of these seem feasible: their use in field emission applications and their inclusion in the production of transparent conductors, interconnects and vias seem most probable. In this paper we will concentrate on their use in field emission applications. Because of their high-current-carrying capability, chemical inertness, physical strength and high aspect ratio, field emission from CNTs can be applied to many technologies. The major applications include their use as electron sources in electron microscopy, as electron sources in portable x-ray systems, in parallel e-beam lithography, in backlighting for AMLCDs, in Field Emission Displays and in propulsion and sensors. All of the above employ CNTs but, for some, single-walled tubes can be utilized, whereas in others multi-walled tubes are more suitable; some can use spaghetti-like CNT films whereas others require aligned arrays.

Carbon nanotubes are composed of sp^2 covalently-bonded carbon in which graphene walls are rolled up cylindrically to form tubes. The ends can either be left open, which is an unstable configuration for field emission due to incomplete bonding. They can also be bonded to a secondary surface, not necessarily made of carbon, or they can be capped by a hemisphere of sp^2 carbon, with a fullerene-like structure [1]. In terms of electrical properties, single-walled CNTs can be either semiconducting or metallic and this depends upon the way in which they roll up. Multi-walled CNTs are non-semiconducting (i.e. semi-metallic like graphite) in nature. Their diameters range from 2 to ~50 nm, and their lengths range from a few 10s of nm to a few mm. Multi-walled CNTs contain several concentric, coaxial graphene cylinders with interlayer spacings of ~0.34 nm [2]. This is slightly larger than the single crystal graphite spacing which is 0.335 nm. Multi-walled CNTs tend to exhibit properties of turbostratic graphite in which the layers are uncorrelated. For instance, in highly crystallized multi-walled CNTs, it has been shown that if contacted externally, electric current is generally conducted through only the outermost shell [3], though Fujitsu have been able to contact the inner walls with resistances of 0.7 k Ω per multi-walled CNT [4].

2 CNT Growth

There are two basic techniques used for CNT synthesis, vaporization of graphite or chemical vapour deposition. There are two vaporization methods: arc discharge [5] and laser ablation [6]. In the arc discharge method, an electric spark between two carbon (usually graphite) rods (typically 100 A) sublimates the carbon in the negative electrode because of the high temperature of the discharge. The vaporized carbon then goes on to form CNTs. Laser ablation involves a pulsed laser that vaporizes a graphite target in a high temperature reactor. Inert gas is bled into the chamber with the CNTs forming on the cooler surfaces of the reactor. The CNTs produced are often coated in layers of amorphous carbon (70% amorphous carbon for arc discharge, 30% amorphous carbon for laser ablation [7]), so a purification step is required to separate the CNTs from the amorphous carbon. CNTs made in this way have been applied to field emission displays, but this synthesis method will not be discussed in detail as our laboratory has concentrated on CVD. The CVD process is a two step process and these are:

- (1) preparation of catalyst nanoparticles and
- (2) growth of the nanotubes by CVD or PECVD (plasma-enhanced chemical vapour deposition), as will be described below.

2.1 Catalyst Preparation

The catalyst metals most commonly used for nanotube growth are Fe, Ni and Co [8]. There are several routes to the production of catalyst nanoparticles, the two main methods being the wet catalyst method and the coalescence of thin catalyst films.

The wet catalyst method involves the deposition of metal nitrate/bicarbonate colloids onto a surface (shown in figure 2a). 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 H_2 and/or thermal decomposition resulting in the formation of metallic catalyst islands from which the CNTs grow [9,10]. The wet colloid method produces an uneven distribution of catalyst particles, but does have a significant cost advantage over vacuum techniques such as sputtering and evaporation.

The most commonly used form of catalyst preparation for devices is coalescence (shown in figure 2c). A thin film (of thickness typically less than 10 nm) of Fe, Co or Ni is deposited onto a substrate by evaporation, sputter coating or electroplating. Upon heating, the thin film breaks up (known as dewetting) to form nanoislands as a result of increased surface mobility and the strong cohesive forces between the metal atoms [11,12]. CNT growth then nucleates from these nanoislands. When grown on silicon and polycrystalline substrates, barrier layers such as ITO,

SiO₂ and TiN are required to prevent diffusion of catalyst into the substrate [13].

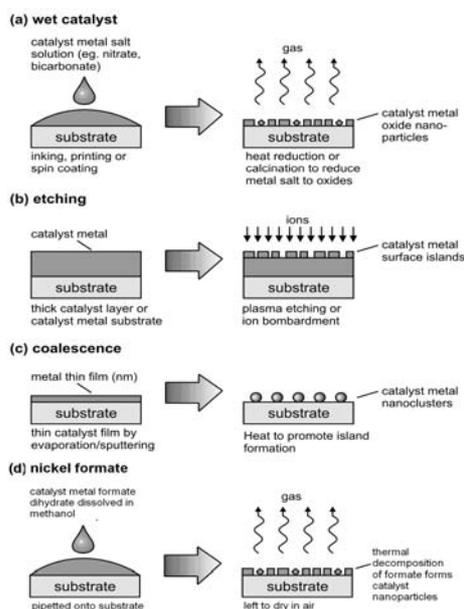


Figure 1. Methods of producing nano-sized catalysts for nanotube growth [14,15,16,17]

2.2 CVD and PECVD Growth

After catalyst nanoclusters have formed, the second step of the process is nanotube growth by CVD or PECVD. This is typically performed using a mixture of a deposition gas (e.g. carbon containing gas such as C₂H₂, CH₄, or CO) and an etching/reducing gas (e.g. H₂ or NH₃) at a temperature of 550 - 900 °C. The deposition gas provides the carbon feedstock for nanotube growth, and early works showed that temperatures in excess of 500 °C are required for the filamentous growth of carbon via catalytic decomposition of the gas and the diffusion of carbon through the catalyst [8]. 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 as a result of the CVD process.

In PECVD, the 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 nanotubes during growth.

Two growth modes, tip or base growth, are possible based on whether the catalyst metal interacts strongly or weakly with the underlying support material. The interaction of the catalyst with the support can be characterized by its contact angle, analogous to 'hydrophobic' (weak interaction) and 'hydrophilic' (strong interaction) surfaces. For example, Ni on TiN or SiO₂ has a contact angle >90° (i.e. 'hydrophobic' or weak interaction) and thus tip-growth is favoured. On the other hand, Co or Fe on Si [16,10] favour base growth. For tip growth, the nanotube length increases with deposition pressure and time as the catalyst is always exposed to the incoming gas/plasma on top. In base

growth, it is common for the nanotube length to saturate soon after growth commences as the catalyst becomes covered by carbon layers or buried beneath a forest of nanotubes [16]. To circumvent this, special substrates such as porous Si are used to ensure that the gases can permeate through to the catalyst [18]. For most applications, tip growth is favoured as the dimensions of the nanotubes can be controlled more accurately.

3. Applications

3.1 Electron Microscopy

Electron microscopy demands a bright, stable, low-noise electron source with a low kinetic energy spread to maximise spatial resolution and contrast. Various groups have investigated the optimum way to produce CNTs for use in microscopy. The most recent detailed analysis was carried out by De Jonge and co-workers and the field emission properties of CNTs collated from all of De Jonge's papers [19] for their use in SEM/TEM sources are summarized below:

Reduced Brightness / (Asr ⁻¹ m ⁻² V ⁻¹)	10 ⁹
Energy Spread / eV	0.25 - 0.50
Short-term stability %	0.2
Running Temp / K	700 - 900
Vacuum Level Requirement / mBar	< 2×10 ⁻⁸
Noise Percentage %	0.12
Virtual source size / nm	0.2

Table 1 Properties of CNT emitters for Microscopy

The CNTs act as a cold cathode source and the standard manufacturing procedure is to add them to the tip of a standard tungsten emitter. Several different methods of attachment/growth have been attempted. De Jonge et al.[20] used a carbon glue to attach the CNT to the tungsten tip but often problems with alignment were encountered as shown in figure 2a. In situ growth, rather than attachment is felt to be a better process. Riley et al.[21] have shown that a forest of highly defective CNTs can be grown on a tungsten tip by thermal chemical vapour deposition (TCVD), but in order for electron beam equipment to work effectively, there must be only a single source of electrons, hence a single CNT on each tungsten tip is required. Mann et al [22] therefore used PECVD with the ability to grow a single CNT on each W tip as shown in fig 2b. It is also possible to grow individual CNTs on many tips simultaneously. El Mul has also developed a silicon-based CNT microcathode in which the CNT is grown in an etched pore [23].

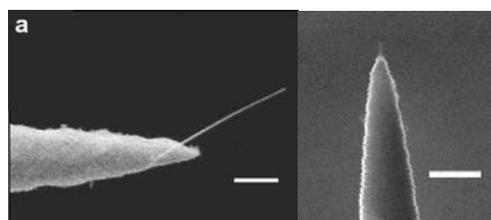


Figure 2 (a) Off-axis attached CNT. (b) on-axis grown CNT. The scalebar is 1 µm in both cases.

The emission characteristics of the CNT have been found to be extremely promising and although the attachment process has been essentially overcome by utilizing PECVD growth there are still problems with stability and reproducibility which are

currently being addressed. Mann et al. [24] recently reported that conditioning – a rapid thermal anneal followed by burning in air - of PECVD-grown CNT tips in the first few hours of emission is key to stabilizing the source.

3.2 X-ray Instruments

Oxford Instruments have worked together with NASA on CNT-based X-ray sources that employ field emission as the electron source, rather than thermionic emission, which has much lower power efficiency [25]. Their application is targeted towards low-power use for a space mission to Mars (though high power would be more preferable), once again because of their low weight and fast response time. Oxford Instruments have also developed and sold hand-held low power X-ray imagers which can be applied to medicine and for diagnostics in circuit boards [26]. Zhou and co-workers at Xintek have developed a fast response, sharp-focus X-ray tube with quick pulsation [27] and MoXtek have also produced similar devices [28]. These devices use films of CNTs deposited on transistor outlines as high emission current densities are not required. More recently an EC funded programme to produce high power hand-held X-ray sources[29] has started where higher powers are required. In this instance the only way to achieve the required electron emission is to use aligned arrays of CNTs (see figure 3) whose separation is approx twice their height [30].

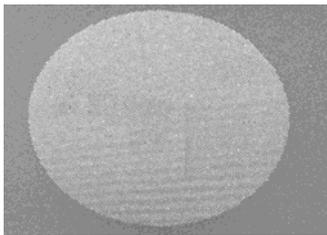


Figure 3 10,000 CNTs grown in a 300 μm diameter circular array in which their separation is twice the height.

3.3 Microwave Amplifiers

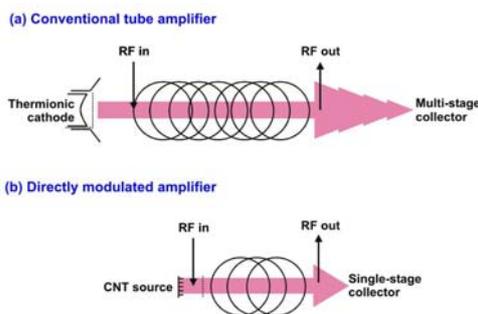


Figure 4: (a) A conventional tube amplifier set-up. (b) amplifier with CNT source

Currently, satellites employ the travelling wave tube (TWT) to produce RF signals. The main elements of a (TWT) are an electron gun, which produces a beam of electrons that travels down a vacuum tube; a magnetic focusing structure that keeps the electrons in a linear path; an RF circuit that causes RF fields to interact with the electron beam; and a collector with which to collect the electrons. This is shown in figure 4.

The helix behaves as a delay line, in which the RF signal travels at the same speed along the tube as the electron beam. The current

in the helix generates an electromagnetic field which interacts with the electron beam. Hence, the current builds up and is thus amplified as it passes down the helix. Conventional microwave amplifiers based on thermionic sources are approximately 30 cm long and weigh 1 kg. An alternative method for microwave amplification [31] incorporates a microwave diode that instead uses a cold-cathode electron source consisting of a CNT array which operates at high frequency and at high current densities. Sixteen CNT arrays individually occupying an area of $0.5 \times 0.5 \text{ mm}^2$ similar to those shown in figure 4 were integrated onto a silicon chip placed on a coaxial post in a resonant cavity.

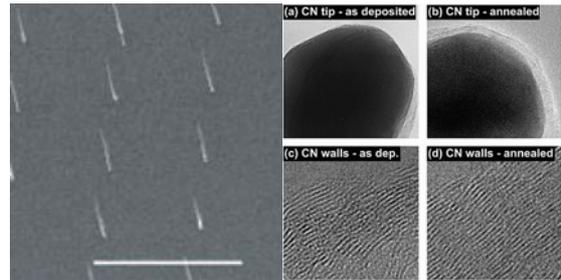


Figure 5: Left, CNT arrays grown on silicon with a spacing of twice the height. Right, CNT tips and walls before and after rapid thermal annealing.

In order to reach the current densities needed for this application the CNTs must also be well crystallized so that they have a high electrical conductivity. So a rapid thermal anneal after growth under high vacuum increases the graphitization of the nanotubes. When such carbon-nanotube arrays are used as the source it emits bunches of electrons directly by turning on and off in response to an input RF signal, in a process known as temporal modulation. There is no need for heating (since carbon nanotubes are cold cathodes), no need for two-thirds of the length of the interaction tube (since the bunches are directly obtained from the carbon nanotubes), and the collector can be simplified as all electrons have the same velocity and fewer electrons are being dumped. It is possible to directly generate RF beams (at GHz frequencies) of electrons from carbon nanotube arrays. 32 GHz direct modulation of a carbon nanotube array cathode under Class A (i.e. sine wave) operation, with over 90% modulation depth obtained. This CNT cathode already delivers average and peak-current densities that are similar to those presently used in microwave transmission devices. The total expected size and weight reduction from the electron source, tube and collector is around 50%. This is highly significant because today, each communications satellite carries around 50 amplifiers. The size and weight savings would lead directly to more devices being carried on each satellite or lighter satellites with cheaper launch costs; it costs £10,000 to send 1 kg into space.

3.4 Displays and Backlighting

Motorola in the early/mid 1990's investigated the use of carbon based materials for Field Emission Displays including the use of diamond, DLC and CNTs [32,33]. More recently they have reported a CNT based Field Emission HDTV [34]. Over the last 10 years or so various companies including Philips, TECO Nanotech, ISE Electronics and especially Samsung (SAIT) [35] have worked on the use of CNTs for TV applications. SAIT successfully produced demos of full colour 39" diagonal TVs and this technology was transferred for production in the mid 2000s. However, no displays based on this technology are yet on the

market.

More work continues on Field Emission displays via SED (Surface conduction Electron-emitter Displays). Formerly a collaboration between Toshiba and Canon, the displays utilise emission from carbon but not CNTs [36]. Most recently, Sony announced a major investment in FEDs based on CNT technology but their plans to start production at a former Pioneer factory in Kagoshima were delayed by financial issues in late 2008 and it was announced in late March 2009 that their spin out company "Field Emission Technologies" was closing down due to the inability to raise capital.

Although their use in full colour TVs is still problematical, the use of CNTs as electron emitters in FE-based backlight units for AMLCDs is still under investigation by various companies worldwide. Major players in the TFT-LCD display industry, such as Samsung, Corning and LG Electronics (LGE), are keen to develop carbon-nanotube (CNT) backlight modules, with Taiwan-based backlight-module makers also interested in following suit [37]. In Korea Iljin also have several years of experience in this area [38].

In theory, CNT backlight modules have a lower temperature, consume less power and are less expensive to produce than traditional backlight modules. It is a good candidate to eventually replace CCFL (cold cathode fluorescent lamp) backlighting but has strong competition from LEDs, which could be much cheaper to produce.

For such applications CNT samples as shown in fig 6 below are sufficient and there is no need to use the complicated lithography to produce the arrays needed for TWT and other high current density applications.

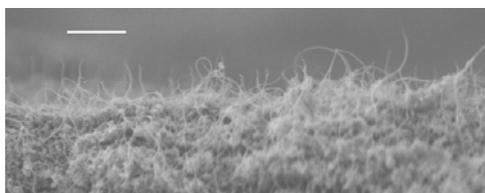


Figure 6. CNTs Used in Backlight Units (scalebar 1 μ m)

4 Conclusions

Although there are continuing problems is using CNTs in Field Emission based Displays there are still numerous applications where field emission from CNTs can be utilized. Their development for use as electron sources in microscopes and for use in microwave sources is still continuing and backlighting, lighting and x-ray source work is still significant worldwide. There still seems to be an excellent outlook for CNT FE applications.

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