Carbon Nanotube Electron Source Technology

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Author's Note: *This article is intended to be an overview of carbon nanotube electron source technology, concentrating on results by the author and his collaborators. It is not intended to be a full review of the field.*

The carbon nanotube embodies a unique combination of properties which make it potentially an extraordinary field emission electron source. These properties include small tip radii (and small source size), high electrical conductivity, high melting point, and resistance to electromigration under an applied electric field. Here, carbon nanotube electron point sources are shown to be remarkably stable, with high brightness, low energy spread, and low noise. These are favorable attributes of an electron source to be used in an electron-optical system. By combining wafer-scale carbon nanotube growth technology with microfabrication techniques, it is possible to mass produce high-performance emitter arrays that can deliver high current beams at high frequencies.

INTRODUCTION

Advances in electron source technology have the potential to profoundly impact a range of applications, from microscopy to telecommunications to electric-propulsion systems for spacecraft. The three most common types of electron sources are the thermionic, cold field emission, and Schottky source. In the thermionic electron source, a material is heated to a high temperature and its electrons gain sufficient energy to overcome the material's work function to be emitted. Common thermionic sources are tungsten wire (operating temperature ~2,400 K), lanthium hexaboride (~1,750 K), or tungsten impregnated with work-function-lowering additives such as barium oxide (~1,000 K).

Thermionic sources produce electron beams with a relatively broad energy spread (~1 eV) and may pose physical constraints in building integrated devices due to their high-temperature operation. In the cold field emission source, a material is subjected to a high electric field (typically a few volts per nanometer) which substantially narrows its electrons' potential barrier to vacuum. The electrons in the material can then quantum mechanically tunnel through this thinned barrier and be emitted. Typically, metals such as tungsten and molybdenum are used as cold field emission sources.

It is immediately apparent that a field emitter could be more power-efficient than a thermionic emitter which requires heating. Field emission sources also offer several attractive characteristics such as instantaneous response to electric field variation, resistance to temperature fluctuation, and high degree of focusability in electron optics due to their sharp (0.2–0.3 eV) energy spread. However, due to the high electric field experienced at the tips of the materials during field emission, the metal atoms often diffuse or electromigrate, causing failure and thermal runaway.

The Schottky emitter, sometimes also referred to as the field enhanced thermionic emitter or thermal field emitter, combines heat (~1,800 K), low work function (tungsten with zirconium dioxide coating), and a moderate applied electric field to create a stable electron source with reasonable energy spreads (0.7 eV). Today, this is the preferred source for use in electron optical applications such as electron microscopy.

THE CARBON NANOTUBE ELECTRON SOURCE

One of the earliest reports of carbon being used as an emission source was by Baker[1] in 1972 who noticed that graphite fibers showed better stability than several metals in a number of environments. Carbon nanotubes are a unique form of carbon filament/fiber in which the graphene walls roll up to form tubes, with diameters typically 1–50 nm and lengths of a few micrometers.[2] Several properties of carbon nanotubes make them favorable for field emission. First, with graphene walls parallel to the filament axis, nanotubes exhibit high in-axis electrical conductivity at room temperature. Second, nanotubes are high in aspect ratio and whisker-like in shape (which, as explained by Utsumi,[3] is the optimal shape for field emission), with a tip diameter of tens or few nanometers (i.e., small point source). Next, nanotubes can be very stable and indeed robust emitters, even at high temperatures due to their strong C-C covalent bonds. Purcell[4] demonstrated that a nanotube emitter, even when heated up by its own field-emitted current to 2,000 K, remains stable. This characteristic is distinctively different from metal emitters.

CHARACTERISTICS OF THE INDIVIDUAL CARBON NANOTUBE ELECTRON SOURCE

Today, individual carbon nanotube sources can be produced on a tungsten needle either by attachment[5] or direct deposition (Figure 1a).[6] Microfabricated sources with an integrated gate, as shown in Figure 1b, can also be produced.[7] The following characterization was performed with carbon nanotubes on tungsten needles. Individual (point) field emission sources are primarily used as electron probes for microscopy or lithography. In these applications, performance parameters such as stability, energy spread, noise, emission pattern, brightness, and current per emitter are important.

The stability of carbon nanotubes, like any other field emitter, is affected by adsorbates, which are residual molecules from the vacuum that adsorb onto the nanotube surface and interfere with the field emission process. Hence, prior to use, it is necessary to quickly heat (i.e., "flash") the emitters to ~900 K to remove the adsorbates before operating them at room temperature.[8] A different strategy is to operate the emitter at high electric field/currents[9] which essentially field evaporates the adsorbates. A clean nanotube emitter then follows the classical Fowler–Nordheim characteristics for field emission,[10] exhibiting a narrow energy spread (0.2–0.35 eV) and high stability. This narrow energy spread is desirable as it improves the focusability of the beam using electrostatic lenses. Under a fixed operating voltage (or field), the typical emission current drift over 1 hour is 0.5%, with short-term peak-to-peak fluctuations of 0.2%[11]—this is a significant improvement over metal emitters, which have an order or more higher instability. The spectral noise content of the emitted current from nanotubes has also been assessed[11] and typical noise percentage values of 0.02% and 0.12% have been measured over frequency ranges of 0.1–25 Hz and 1 Hz–10 kHz, respectively, which is comparable to values obtained for the state-of-the-art Schottky emitter. These frequency ranges are of interest as they correspond to the typical slow and fast scan rates used in an electron microscope. The noise values have been verified over a range of emission currents (0.1–2 μA) and only increase when the vacuum level degrades to 10^{-8} Torr or higher,[11] most probably due to the effect of adsorbates. One should note that by operating nanotube emitters slightly warm (~700–800 K), it is possible to prevent re-adsorbation and hence improve overall stability, with negligible increase in the energy spread.

Table I. Typical Properties of Various Types of Electron Sources

Property	Thermionic (Tungsten/LaB_6)	Schottky (Tungsten+ZrO)	Metal Cold FE (Tungsten)	Carbon Nanotube FE*
Virtual Source Size (nm)	10,000	<20	<10	<10
Energy Spread (eV)	1	0.7	0.2–0.3	0.2–0.35
Brightness (A/m^2srV)	10^6-10^7	10^8	10^8	10^9
Stability (%)	<1	<1	4–6	<0.5
Operating Temp.	1,500–2,100°C	1,500°C	25°C	25°C–400°C*
Lifetime	100–1,000 hours	>1 year	>1 year	>1 year

* For the carbon nanotube field emission source, it can either be operated at room temperature (25°C) or slightly warm (400°C) to prevent re-adsorbtion of residual molecules in the vacuum and enhance its stability. Even when hot, carbon nanotubes, which are covalently bonded, remain stable and do not suffer from diffusion/electromigration like metal emitters.[4]

Two common types of capping structures on nanotube tips exist—open and closed—and both of these have been assessed in terms of current, stability, and emission pattern. An open tube offers a sharp edge to an applied electric field, thereby producing a higher field enhancement and obtaining a higher current for a fixed applied voltage than a closed nanotube. However, the open nanotube actually has poorer stability and an emission pattern consisting of dispersed or widely spaced spots, which sometimes even move with time.[12] The poor stability of the open nanotube arises from the dangling bonds that exist at the open end of a nanotube. Thus, the closed nanotube is more desirable as this structure produces excellent current stability and a smooth emission pattern,[12] from which a useful electron beam may be extracted. Open nanotubes are known to spontaneously close during field emission—and remain closed thereafter.[12] Due to their smooth hemispherical tip, the field enhancement of closed nanotubes tends to agree with whisker theory, allowing the emitters to be effectively modeled.[3,10,13]

The maximum current per carbon nanotube emitter is typically 5–10 μA. The failure of carbon nanotubes is abrupt, and post examination often reveals that a crater has formed due to excessive heat or the nanotube has disappeared from its location (i.e., electrostatically separated from its contact). One should note that these types of failures are sudden and differ significantly from the gradual thermal runaway/electromigration of metal field emitters or the failure of thermionic emitters. The lifetime of a thermionic emitter depends on its operating temperature, which in turn determines the emission current density. Thus, a thermionic emitter could be operated at a lower current density or temperature to improve its operating life. In contrast, nanotube emitters appear to have a long (i.e., years) life at currents below a certain threshold (5–10 μA), above which they appear to instantaneously fail as described previously. This failure current can be increased up to 100 μA by rapid thermal annealing of the nanotube at 1,200 K.[14] The annealing process crystallizes the nanotube, decreases its bulk resistance, and reduces any contact resistance. This decreases any voltage drops and heat generation across the nanotube during field emission. A further possibility is that the annealing leads to metal-carbide formation[15] at the nanotube-contact interface which enhances the adhesion of the nanotube, allowing it to operate under higher applied electric fields.

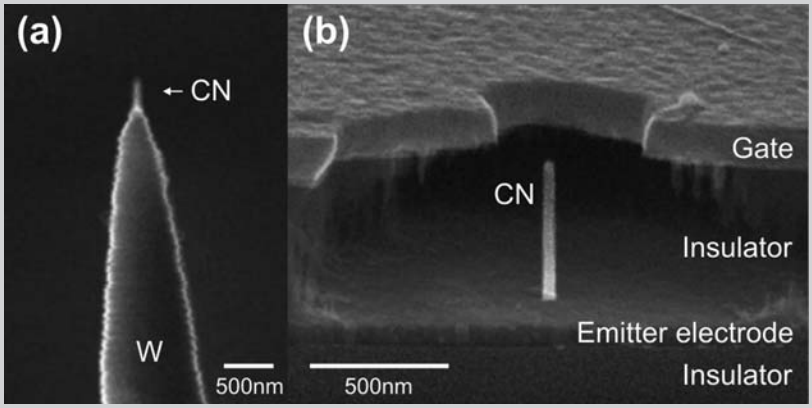

Figure 1. Individual carbon nanotube field emitter electron sources. Vertical carbon nanotubes (CN) can be deposited directly onto (a) tungsten needles or in (b) gated apertures.

Table I compares the nanotube electron source with the thermionic, Schottky, and metal (tungsten) field emission source. The tungsten cold field emission source is used in applications where heat is a problem or where very small energy spreads are required. However, it is applied at the expense of poor stability. The Schottky source offers excellent stability at the expense of energy spread and heat. The nanotube field emitter, which has the same stability and noise as the Schottky source, delivers a high-brightness electron beam with narrow energy spread and is a contender as a source for electron optical applications.

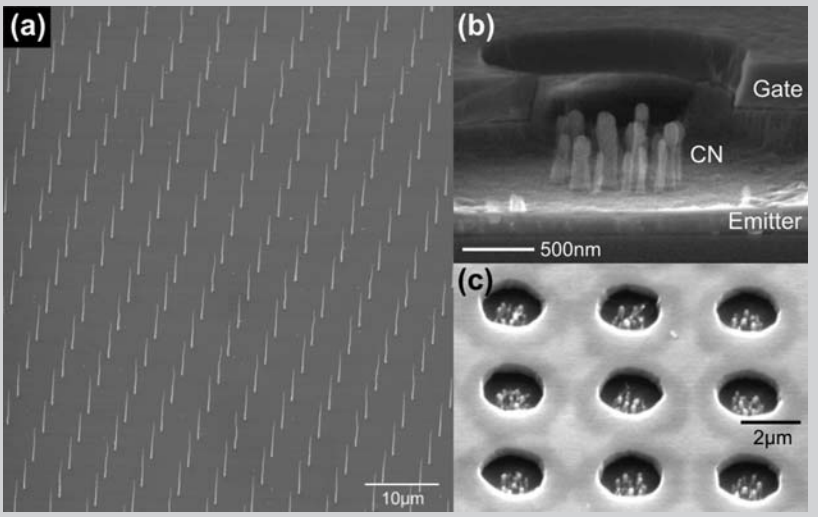

Figure 2. (a) An array of vertically aligned carbon nanotubes. (b) A cross section of a gated field emission source containing multiple carbon nanotubes (CN). (c) An array of gated apertures forming a large area electron source.

CHARACTERISTICS OF THE CARBON NANOTUBE ARRAY ELECTRON SOURCE

Field emitter arrays can either be in the form of free-standing arrays (Figure 2a) on a substrate or an ensemble of gated emitters (Figure 2b and c). These electron sources are, in general, used in applications that require high currents, fast response, or large areas. Applications include sources for microwave amplifers,[16] pulsed x-ray sources,[17] field-emission displays,[18,19] electron impact ionizers for gas detectors, or neutralizers for ion space-thrusters.

In carbon nanotube field emitter arrays such as those shown in Figure 2a, the optimal emitter spacing to emitter height ratio has been determined to be 2:1.[20] When emitters are placed closer than this, the field enhancement at the tips of the emitters is reduced due to the electrostatic shielding from adjacent emitters, subsequently decreasing the emission current density for a certain applied electric field. If emitters are placed further apart than the optimal ratio, the density of emitters is reduced which also decreases the emission current density for a certain applied electric field. A gate or grid electrode is usually placed tens to hundreds of micrometers above the array to supply the electric field for field emission.

In applications such as field emission displays, it is desirable to have as low an operating voltage as possible. To achieve this, one must reduce the gate-to-emitter distance, since the applied electric field is inversely proportional to the distance. Microfabricated nanotube emitters with an integrated gate, such as those shown in Figures 1b and 2b and c, allow this to be achieved. These two devices, fabricated by Thales and Cambridge, exhibit typical operating voltages of 20–40 V with four orders of change in emission current over this region.[7,21,22] As the fabrication is on planar substrates using conventional microfabrication, the manufacture of a large number of gated emitter arrays over wafers or glass substrates is possible.

The integrated gate, however, poses a problem for high-frequency operation because it has a large capacitance due to its close proximity (1 μm or less) to the emitter electrode and the dielectric insulator. This limits the operation of most integrated devices to the kilohertz or megahertz range. To operate nanotube emitters in the gigahertz range, we revert to the free-standing nanotube arrays of Figure 2a with a vacuum gap to a grid/gate tens of micrometers away (i.e., much lower capacitance).

Microwave (GHz) devices, such as amplifiers used in radar and satellite telecommunications, currently utilize thermionic sources to generate their electron beams in direct current (d.c.), which are modulated and amplified downstream in vacuum tube devices. The modulation process and hot cathodes result in physically long electron tubes. Moreover, at high frequencies, the modulation process is inefficient and only part of the beam is modulated. It is currently not feasible to directly generate a radio frequency (RF) beam of electrons from the thermionic source as its high operating temperature gives rise to physical constraints of placing a grid in close proximity to the source, and the thermionic process leads to rather low-energy, slow electrons with a long transit time.

In contrast, it is possible to directly generate RF beams (at gigahertz frequencies) of electrons from carbon nanotube arrays. Working with Thales, Class D (i.e., pulse mode/on-off) operation of a carbon nanotube array cathode at 1.5 GHz was recently demonstrated, with an average current density of 1.3 A/cm^2 and peak current density of 12 A/cm^2;[16] these are compatible with traveling wave tube amplifier requirements (>1 A/cm^2). Recently, a 32 GHz direct modulation of a carbon nanotube array cathode was achieved under Class A (i.e., sine wave) operation, with over 90% modulation depth. This unique ability to directly modulate or generate RF/GHz electron beams from carbon nanotube emitters is especially important for microwave devices as it essentially replaces the lengthy hot cathode and its associated modulation stage. Other advantages that the carbon nanotube cathode offer include no heating requirement and the ability to turn it on or off instantly (for efficient operation).

FABRICATION OF CARBON NANOTUBE ELECTRON SOURCES

The enabling technology behind the fabrication of carbon nanotube electron

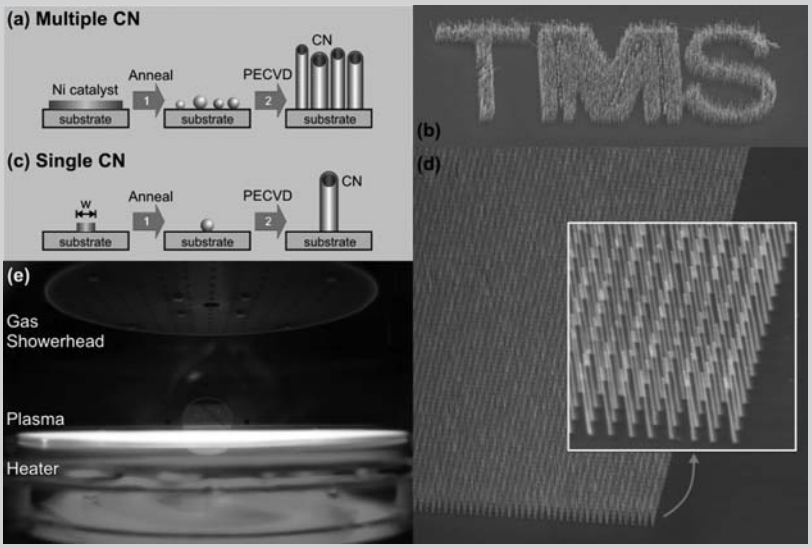

Figure 3. (a) The deposition process for multiple carbon nanotubes (CN), an example of which is shown as the TMS logo in (b). (c) Deposition process for individual carbon nanotubes, where w <300 nm typically, leads to uniform arrays as shown in (d). A wafer-scale (6-inch) carbon nanotube plasma enhanced chemical vapor deposition reactor is shown (courtesy of *www.nano-inst.com*).

sources is the controlled growth of carbon nanotubes. The growth technique on which this work focused is plasma-enhanced chemical vapor deposition.[23,34] A patterned catalyst film (usually nickel) is first deposited onto a substrate. The growth process, which consists of two steps as shown in Figure 3a, is then performed. During catalyst anneal (step 1), the catalyst film transforms into nanoclusters. The size and density of the nanoclusters depend on the annealing speed, time, and final temperature as these factors affect the surface mobility of the nickel atoms in the film. Deposition (step 2) is performed using plasma-enhanced chemical vapor deposition of acetylene and ammonia. In this process, the acetylene provides the carbon feedstock for nanotube growth, whereas the ammonia etches away unwanted amorphous carbon deposits, producing 'clean' growth.[25] The plasma creates an electric field perpendicular to the substrate during growth and is responsible for the vertical alignment of carbon nanotubes.[24] The growth of carbon nanotubes is highly selective; that is, nanotubes are only nucleated on the catalyst. For example, a catalyst pattern with the letters 'TMS' leads to a forest of nanotubes grown in the patterned areas only (Figure 3b). By controlling the catalyst anneal and the size of the nickel patterns, it is possible to obtain individual nickel nanoclusters which nucleate individual nanotubes with highly uniform heights and diameter as depicted in Figure 3c and d.[26] The use of self-assembly or imprint lithography[27] enables the fabrication of large area nanotube arrays. The growth process used yields closed emitters that are highly desirable as emitters for reasons mentioned previously. Emitters are then rapid thermal annealed under high vacuum conditions to improve crystallinity and adhesion. This carbon nanotube deposition process is wafer or tungsten needle compatible and scalable, and commercial equipment has been developed, as shown in Figure 3e.[28]

CONCLUSIONS

Carbon nanotubes have several unique material properties that make them attractive candidates for field emission electron sources. Currently, under lab tests, individual carbon nanotube field emitters can produce high-brightness, stable, low-noise electron beams with narrow energy spread. Carbon nanotube emitter arrays can deliver electron beams with high current densities at high frequencies, and low voltage sources can be fabricated by integrating a gate around the nanotube emitter. Furthermore, the nanotube growth technology used is scalable and allows the deposition of nanotubes onto a variety of useful emitter structures. Carbon nanotubes are indeed a promising material for next generation electron sources.

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