Field Emission of Carbon Nanotubes

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Abstract

Carbon nanotubes , a novel form of carbon discovered in 1991, have been rapidly considered as one of the most promising electron field emitters. Their potential as emitters due notably to the very good field emission stability compared to metalic emmiters in various devices has been amply demonstrated during the last five years . Different types of nanotubes show significant differences in emissions. To obtain good performances as well as ling emitter life times, the nanotubes should be multiwalled and have closed tips. Complementary results such as field emission, energy distribution give indications on the emission mechanism. Comparison between nanotube films at different densities, degradation and field emission mechanism is discussed here.

1 Introduction

In 1991, Iijima discovered closed tabular structures consisting of nested cylindrical graphitic layers capped by fullerene-like ends with a hollow internal cavity.

Imagine taking a sheet of graphite, a simple planner assembly of carbon atoms disposed in a honeycomb lattice, and rolling it up to form a cylinder. These cylindrical structures are called carbon nanotubes and they show exceptional electronic and mechanical properties. They are flexible but very hard to stretch and have extremely low turn-on fields and high current densities ranking them among the best electron field emitters that are available today.

Carbon nanotubes consists of either one cylindrical graphene sheet (single-wall nanotube (SWNT)) or of several nested cylinders with an interlayer spacing of 0.34-0.36nm(multiwall nanotube (MWNT)). The lengths of SWNTs and MWNTs are usually well over 1μm and diameters range from $\sim$1nm (for SWNTs) to $\sim$50nm (for MWNTs). SWNTs are usually closed at both ends by fullerene-like half spheres that contain both pentagons and hexagons [1].

There are different ways of forming a cylinder with a graphene sheet [1]. A few configurations are shown in figure (2). If you roll up the sheet along one of the symmetry axis this gives either a zigzag tube or an armchair tube. It is also possible to roll up the sheet in a direction that differs from a symmetry axis to obtain a chiral nanotube in which the equivalent atoms of each unit cell are aligned on a spiral. These different types of nanotubes can be defined by a chiral angle θ (see fig 1), where chiral angle is the angle it makes with respect to the zigzag direction.

A SWNT with a well-defined spherical tip, a closed MWNT and an open MWNT where the ends of the graphene layers and the internal cavity of the tube are exposed can be seen in the figure given (see next page) . The shape of the cap of the closed MWNT is more polyhedral than spherical.

The defects of the hexagonal lattice are usually present in the form of pentagons and heptagons. Pentagons produce a positive curvature of the graphene layer and are mostly found

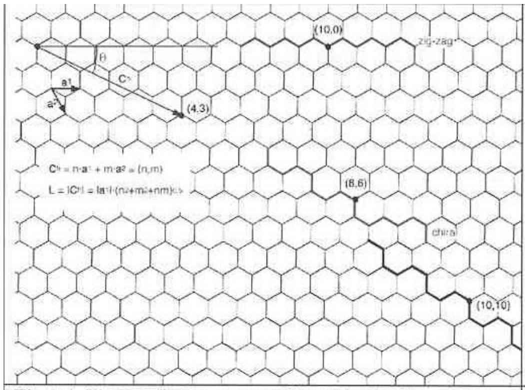


Fig 1:A "de Heer" abacus: to realize a (n,m) tube, move n times a1 and m times a2 from the origin to get to point (n,m) and roll-up the sheet so that the two points coincide...

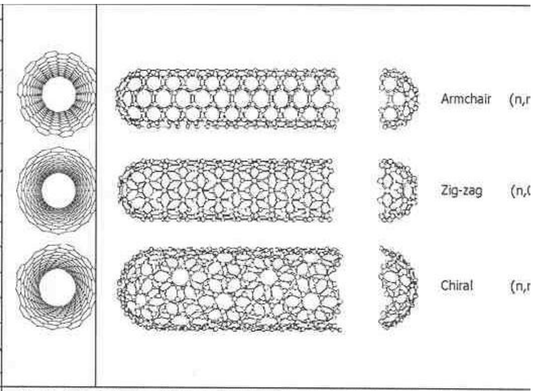


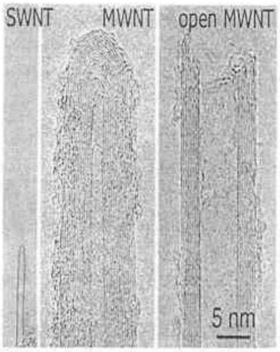
Fig 2: Models of different singlewall nanotubes (generated with. . Mathematica on the left, and taken from Saito et al., APL 60,. . 22 (1992) on the right).

at the cap as in Fig 2(b) where each knick in the graphene layer points to the presence of pentagons in the carbon network. Heptagons give rise to a negative curvature of the wall.

2.1 Field Emission Basics

Field emission involves the extraction of electrons from a solid by tunneling through the surface potential barrier . The emitted current depends directly on the local electric field at the emitting surface E, and on its work function,ϕ.

De Heer, Andre Chatelain and Daniel Urgate first proposed the use of nanotubes as a field emitter in 1995. Field emission is important in several areas of industry, including lighting and displays and the relatively low voltages needed for field emission in nanotubes could be an advantage in many applications.



Transmission electon microscory (TEM) pictures of the ends of different nanotubes. Each black line correspond to one graphene sheet viewed edge-on.

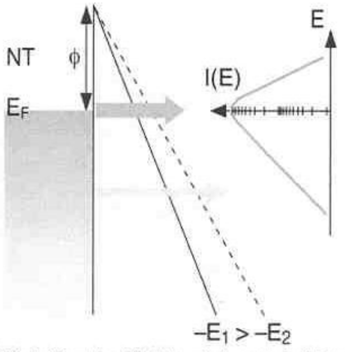


Fig1: Standard field emission model from a metallic emitter, showing the potential barrier and the corresponding energy distribution (energy on the vertical axis, current on the horizontal logarithmic axis).

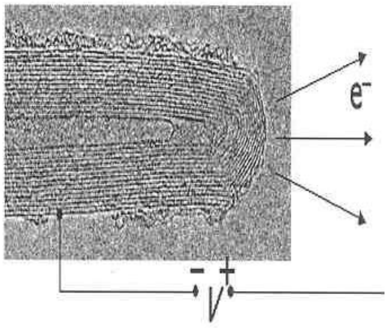


Fig2: Typical set-up for field emission: a potential difference is applied between a nanotube (or an assembly of nanotubes) and a counter electrode.

Fowler-Nordheim model shows that the dependence of the emitted current on the local electric field E and the work function ϕ, is exponential like. As a consequence, a small variation of the slope or surrounding of the emitter and/or the chemical state of the surface has a strong impact on the emitted current.

The small diameter of carbon nanotubes is very favorable for field emission, the process by which a device emits electrons when an electric field or voltage is applied to it.

The field E has to be very high, in the order of $(2-3)\times10^7$V/cm. To reach this value, we take advantage of the field amplification effect: The electric field lines are concentrated around a sharp object. As the field amplification increases with decreasing radius of curvature, the sharper the better. Nanotubes are thus ideally suited as field emitters, as their elongated shape ensures very high field amplification.

2.2 Emitter Characteristics

2.2.1 Single Nanotube Emitter

At low currents the I-V characteristics follows a Fowler-Nordheim (F-N) behavior (i.e. Elastic tunneling through a triangular barrier, with the electron distribution described by Fermi-Dirac statistics, which describes quite accurately electron field emission from metallic emitters). A constant slope in such a plot characterizes a F-N behavior. Depending on the sample the metallic behavior persists up to 5-20 nA of emitted current. At higher currents, the slope changes (by typically 10%-30%) increasing or decreasing depending on the sample, without discontinuities or instabilities in the I-V characteristics up to 0.1μA. A very strong saturation with large instabilities followed by an abrupt step was sometime observed when the voltage was further increased.

Most single MWNT emitters closed as well as open are capable of emitting over an incredibly large current range. The maximum current drawn from one nanotube was ~0.2mA and MWNT can draw currents of 0.1mA, representing a tremendous current density for such small objects.

Except for the voltage needed for electron emission there exist no significant difference between closed and open MWNT. Open tubes are far less efficient emitters than closed ones. Thus emission characteristics of nanotubes are seriously degraded by opening their ends with the voltage needed typically a factor 2 higher for open tubes. This was surprising because the smaller effective curvature of the open nanotubes was expected to lead to larger field amplification. It is now thought that other species (such as Oxygen atoms) attract themselves to the free dangling bond at the ends of the nanotube, resulting in a localized electron states. Since these states lie well below the fermi energy in the nanotube, they can not emit electrons. Localized states are also thought to form at the tips of closed nanotubes. However these states couple to so called π-orbitals in the nanotube and this effectively enhances the emission of electrons.

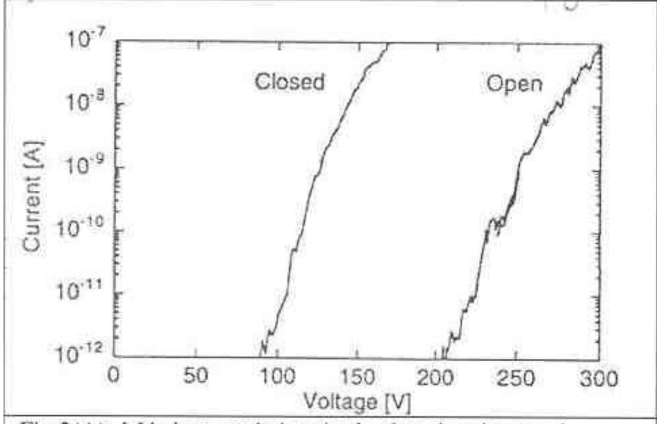


Fig 3(A): I-V characteristics single closed and opened MWNT (current in logarithmic scale).

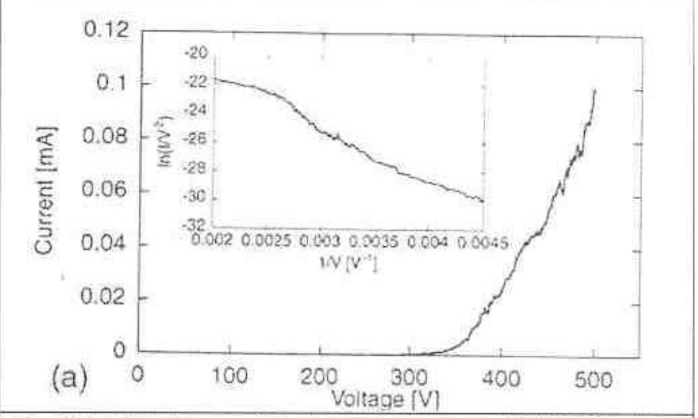


Fig 3(B) : I-V characteristics for a single opened MWNT. (within inset the corresponding Fowler- Nordheim plot)

Nanotube Film Emitters

The behavior of film is readily comparable to the single emitters, as can be seen in Fig 4(b) for a SWNT film. At low currents, Fowler-Nordheim behavior was observed up to emitted

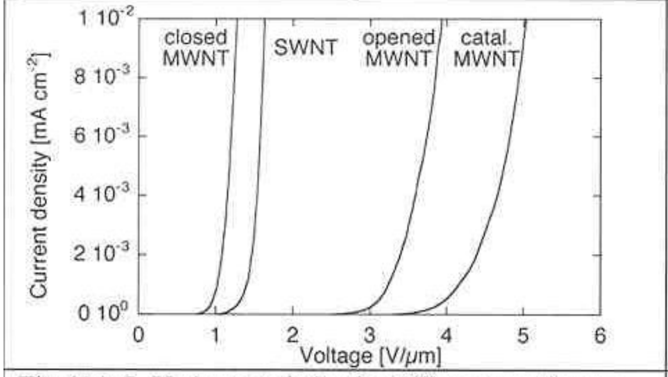


Fig 4(a) :I -V characteristics for different continuous nanotube films. From Bonard et al., Appl. Phys. A69, 245 (1999)

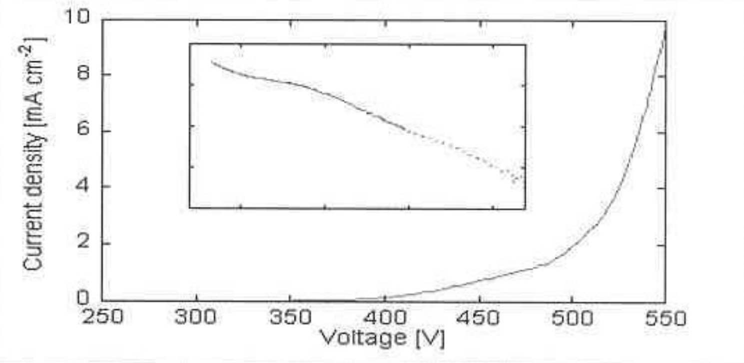


Fig 4(b): I-V characteristics for a SWNT film with in inset the corresponding Fowler_Nordheim plot. Solid and dotted lines correspond to different ranges of the source-measure unit.

current densities of 0.1-10μAcm^{-2}.with the F-N slope changing slightly at higher currents. At 10-100μAcm^{-2}, a distinct diminution of the F-N slope (and therefore saturation) occurred on all samples.

According to fig 4 closed MWNT films display lower emission voltages followed by SWNT, opened MWNT and finally catalytic MWNT. With tubes aligned with their axis perpendicular to the substrate, high field amplification at the nanotube tips and thus in lower operating voltages are observed.

2.3 Comparison between Nanotube films of Different Densities

Density and the length of the nanotube influence the macroscopic field emission. The best and the worst field emitters are the films with medium and low densities respectively.

The low-density sample shows a rather inhomogeneous emission pattern with very few sites emitting a low current. The turn on fields for low density films are high because there are few emitters with short heights.

A high nanotube density yields a result similar to the low density one, albeit with an emission intensity higher by a factor of 10. The decreased quality results from a combination of two effects; the inter-tube distance and the number of emitters. When the inter-tube distance is large the field amplification factor is determined only by the diameter and the height of the tube. As the distance between the tubes is decreased, screening effects become significant. The height if the nanotubes over the substrate is also important for good emission. Therefore the emission from the high density films is more efficient but remains low because of screening effects between densely packed neighboring tubes and because of small heights of the tubes.

A much more homogeneous emission image is obtained for a medium density primarily due to a large no of emitting sites. Here the lengths of the tubes and the distance between neighboring emitters are both sufficient to reach high field amplification along with an emitter density that is high enough to ensure homogeneous emission at low voltages.

2.4.1: Energy Spread

Energy spread for field emission electron sources are far lower than for thermo-electronic sources, in fact they are comparable with ultra sharp emitters where the emission occurs from well-defined emitting states as opposed to metallic continuum. The figure shows a typical energy distribution obtained on a closed MWNT film. The FWHM (full width at half maximum) is observed to be ~0.2 eV. The energy spread of MWNTs is thus at least half that of metallic emitters.

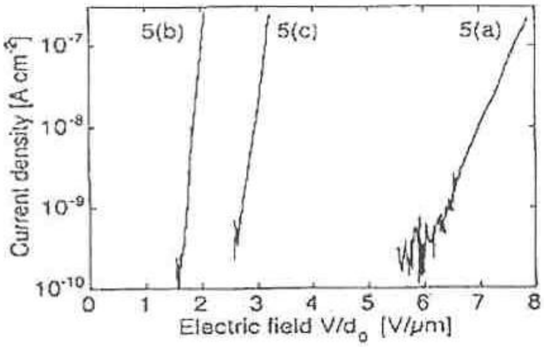


Fig 5: Field emission I-V curves of MWNT films of different densities. The left, middle, and right characteristics were acquired for medium, high and low densities.

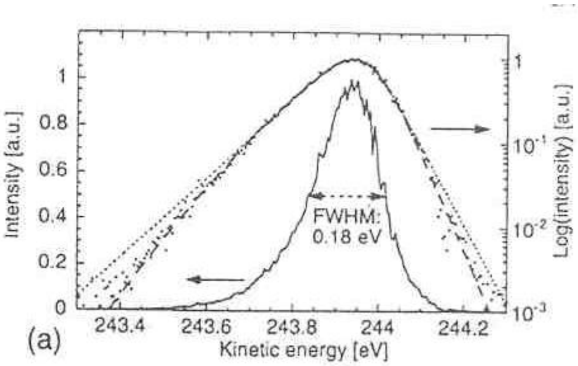


Fig 6: Field electron energy spectra obtained on a MWNT film along with the F-N distribution (dotted line) and with the modified F-N distribution including a Gaussian band of states.

Electron field emission from metallic emitters can be described quite accurately using Fermi-Dirac statistics (Fowler-Nordheim theory). The curve in dotted lines shows the spectrum for this F-N distribution. To obtain good agreement with the measured spectra using a Gaussian band of states at the tip of the tubes (instead of the usual metallic density of states) results in a distribution such as the one shown in the dashed line. This is in fact the Fowler-Nordheim distribution times a Gaussian band of width δE centered at an energy E$_c$. with this distribution, the tube body that supplies the tip states (Gaussian bands) with electrons is taken as metallic, i.e. a DOS described by the Fermi-Dirac statistics.

The shape of the energy distribution of MWNTs therefore strongly suggests that the electrons are not emitted from metallic continuums, but from energy bands of 0.2-0.4 eV widths.

2.4.2 : Field Emission Mechanism

Large field amplification factor, arising from the small radius of curvature of the nanotube tips, is partly responsible for the good emission characteristics. It is however still unclear whether the sharpness of the nanotubes is their only advantage over other emitters, or if intrinsic properties also influence the emission performances.

If the nanotubes seem to follow the Fowler-Nordheim law they can be thought of as metallic emitters. As discussed in chapter (2.4.1) nanotube emissions, deviate from Fowler-Nordheim model. Such deviations are usually attributed to space-charge effects, which induce a diminution of the f-N slope at high fields. Thus nanotubes cannot be considered as usual metallic emitters. Also for nanotubes electrons are not emitted from a metallic continuum as in usual metallic emitters, but rather from well defined energy levels of ∼0.3 eV half width corresponding to localized states at the tip .The energy spread of nanotubes is typically half that of metallic emitters (∼0.2). And the shape of the energy distribution suggests that the electrons are emitted from narrow energy levels. Greatest part of the emitted current comes from occupied states with a large density of states near the Fermi level but the other deeper levels also contribute to the field emission.

The greatest part of the emitted current comes from occupied states below the Fermi level. The position of these levels the with respect to the Fermi level, which depends primarily on the tip geometry (i.e. tube chirality, diameter and the eventual presence of defects), would be, together with the tip radius are the major factors that determines the field emission properties of the tube. Finally it is worth noting that the presence of localized states influences the emission behavior greatly. Local density of states at the tip reaches values at least 30 times higher than in the cylindrical part of tube increasing the carrier density for strong emission.

3.1: Conclusion

Carbon nanotubes possess small radius of curvature at the tip, high mechanical strength all of which are favorable for field emitters.

To obtain low operating voltages as well as long emitter lifetimes, the nanotubes should be multi-walled and have closed, well-ordered tips .The SWNTs degrade substantially faster. And it was observed that opening their ends seriously degrades emission performances of MWNTs. The large field amplification factor arising from the small radius of curvature of the nanotube tips, is partly responsible for the good emission characteristics. It can be concluded that the density of states at the tip of carbon nanotubes is non metallic, appearing in the form of localized states with well defined energy levels and that the presence of such states influences greatly the emission behavior.

3.2: Applications

Applications of single MWNT

Low energy electron projection microscopes have been developed where the electrons are extracted by applying a voltage between the sample and a MWNT emitter. Here the nanotube provides a highly coherent beam that allowed the acquisition of in-line electron holograms of the observed objects with a quality comparable to atom sized W emitters.

Nanotube emitters show high coherence, high current density and narrower FEED (Field Emission Energy Distribution) than cold or Schottkey cathodes, which are used in instruments like scanning or transmission electron microscopes. However it has not been proven yet that single nanotubes can be used in such instruments.

Applications of Assembly of Nanotubes

In contrast to single nanotube devices, applications based on an assembly of nanotubes are diverse.Nanotube flat panel displays are used as alternative to other film emitters. Matrix addressable pixels in diode configurations have been developed as example. Recently a fully scaled 4.5 inch, 3 color, field emission display with 128 addressable lines which works in diode configuration have been developed

Nanotubes can be used in lighting elements (i.e. to produce light) by bombarding a phosphor-coated surface with electrons. The brightness is higher by a factor of 2 as compared to conventional thermionic lighting elements used for giant outdoor displays.

Field emitters are also of great interest for microwave amplification. This type of application is very demanding because the current density must at least be 0.1 A/cm2.

Gas discharge tubes has also been developed as an over voltage protection. When the voltage between a nanotube cathode and a counter electrode reaches a threshold value for field emission, the emitted current induces a discharge in the noble gas-filled inter electrode gap.

References

[1] Saito R.,Fujita M.,Dresselhaus G. and Dresselhaus.S.,Appl Phys Lett **68**,1579 (1992).

[2] Bonard J.-M., Kind H., Stöckli T. and Nilsson L-O., Solid-State Electronics **45**,893-914 (2001).

[3] Bonard J.M., Salvetat J.-P.and Stöckli T., Appl. Phys. A. **69**,245-254 (1999).