FIELD EMISSION FROM ARRAYS OF CARBON NANOTUBES

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ABSTRACT

The field emission properties of carbon nanotube arrays grown by CVD methods are reviewed. The effect of nanotube length on the emission is explored, and the effect of mutual shielding in dense carbon nanotube arrays is recognized. Ongoing efforts to optimize the emission site density are also underway.

BACKGROUND & THEORY

Thermionic emission has been the standard cathode technology for many years. However, the requirement to heat the cathode to near 1000C limits the ways in which these cathodes can be used, and is a constant power drain on the system. Field emission is an alternative process where electrons tunnel out of a material under the influence of an intense electric field. In the illustration below, Figure 1, electrons overcome the potential barrier at the nanotube-vacuum interface, and are emitted into vacuum. A three electrode or "triode" configuration is shown, which has certain advantages for some field emission devices.

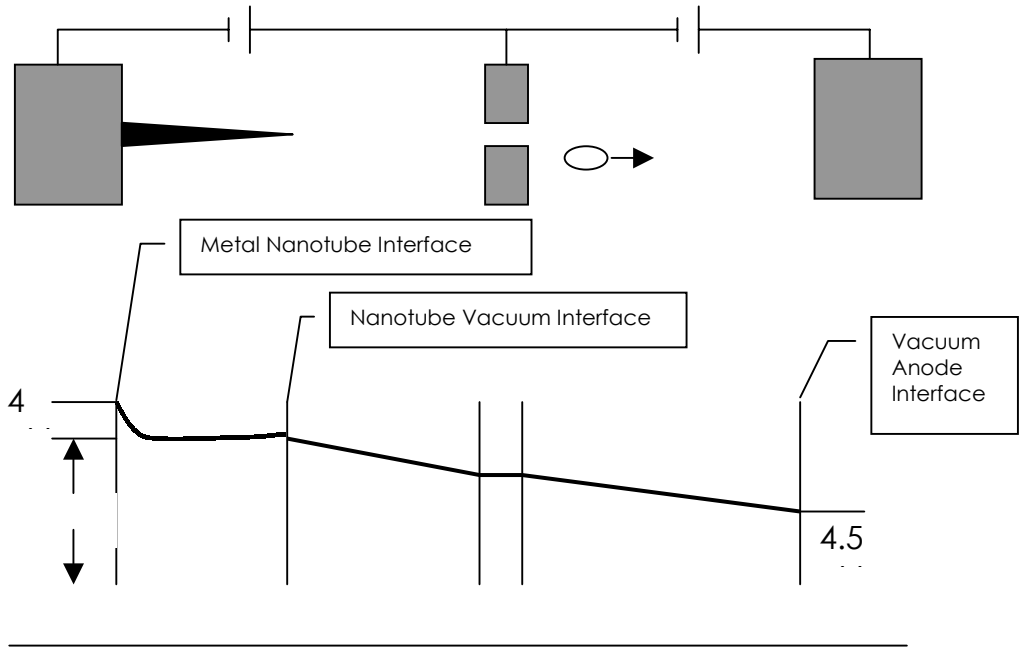


Figure 1. Under electric field, electrons tunnel from the material into vacuum.

Because high electric fields are required to overcome the potential barrier, studies have focused on the identification of low work function emitters and also geometric methods of enhancing the field. The formation of needle-like tips at the surface of the cathode material is the primary method to achieve geometric field enhancement. The electric field is expressed as voltage per unit distance (E=V/d) for planar electrodes. But when a needle is used, the field also depends on the tip radius (V/r). We define the field intensification factor "γ" as the inverse of the tip radius, so the electric field can be written as:

$$E = \left(\frac{1}{r}\right)\frac{V}{d} = \frac{\gamma V}{d}$$

Field emission follows the relation proposed by Fowler and Nordheim, as follows,

$$J = \frac{AE^2}{\phi}\exp\left(\frac{-B\phi^{3/2}}{E}\right)$$

where J (A/m2) is the current density, and ϕ is the work function. A and B are constants, having values of 1.54×10^{-6} and 6.83×10^{9}, respectively. Together, the Fowler-Nordheim equation takes the following form:

$$\frac{J}{V^2} = \frac{1.54 * 10^{-6}\gamma^2}{\phi d^2}\exp\left(\frac{-6.83 * 10^{9}\phi^{3/4} d}{\gamma V}\right)$$

To plot this expression, a linear relationship is obtained by utilizing the 'Fowler-Nordheim coordinate" relationship. Therefore, we can discriminate between field emission and thermionic or other currents observed during tests. If the current is due to field emission, the current-voltage characteristic will be a straight line when ln(y) is plotted against x:

$$\ln y = \ln\left(\frac{1.54 * 10^{-6}\gamma^2 A}{\phi d^2}\right) - 6.83 * 10^{9}\frac{\phi^{3/4} d}{\gamma} x$$

where x is the inverse of the voltage, and y is the product of current density (J) and area (A) divided by the square of the voltage (JA/V^2). It is useful to note that the area of the emitter can be determined exactly, if the work function is known.

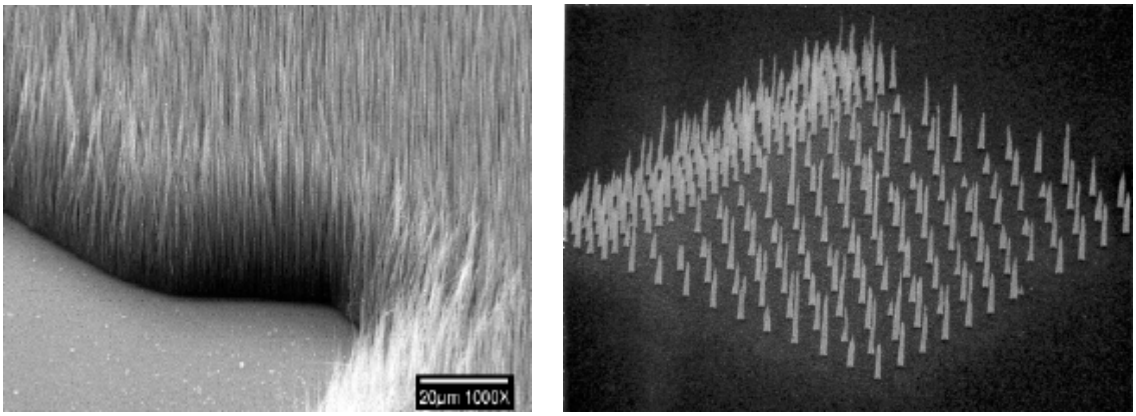
NANOTUBE GROWTH

The high conductivity of nanotubes, combined with their small diameter and robust structure makes them attractive for field emission cathodes. Unfortunately, the production processes for nanotubes resulted in tangled, uncontrolled nanotube clusters that were difficult to disperse, align and obtain acceptable emission properties.

However, after a key discovery in 1998 by Dr. Ren at the University of Buffalo, a new process allowed the direct synthesis of aligned nanotubes on a substrate. The fabrication of these array is reviewed elsewhere.[1] After the patent issued, NanoLab licensed this

[1] Science 282, Well Aligned Carbon Nanotube Arrays on Glass, Vol 7 1105 (1998)

technology, and is now working to develop field emission devices with enhanced properties.
The aligned nanotube fields are grown on a silicon substrate, as shown in Figure 2A, which shows a dense field of 20 micron length nanotubes. In Figure 2B, a patterned nanotube array has nanotubes roughly two microns in length, separated by 2 microns in the low density region of the array, and spaced by 1 micron in the high density region. The growth of nanotubes occurs only where the catalyst is present, and there are a number of highly controllable variables that can be used to tailor the nanotube morphology.

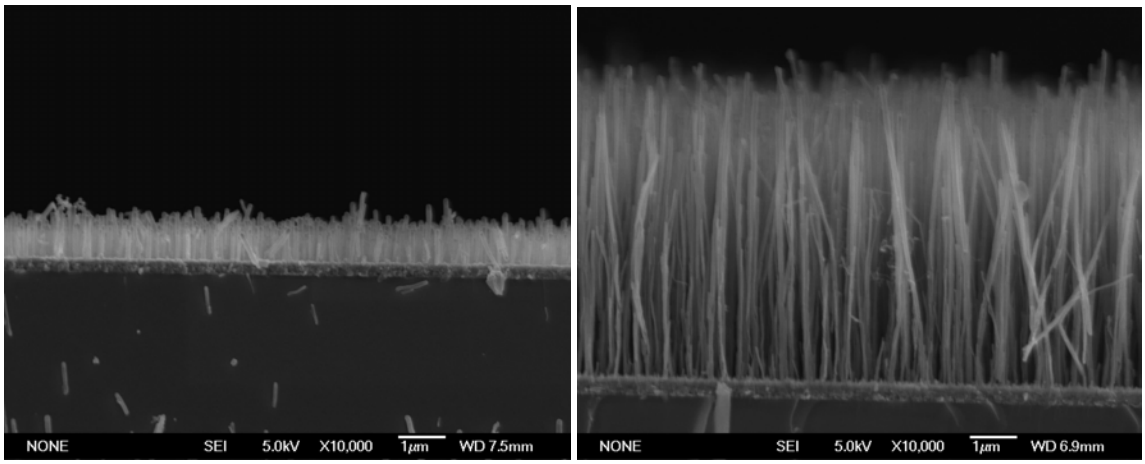


(A) (B)

Figure 2A,B. Nanotube arrays grown by CVD can be uniquely tailored for various applications

RESULTS

To date, we have grown dense aligned arrays and tested their emission properties. Two emitters are shown on edge, in Figure 3A and 3B. The nanotubes have been grown to 1, 3, 5, and 13 micron lengths. Note that there is some height variation between nanotubes in the 5 micron image. This variation causes the longer nanotubes to be more emissive than the shorter ones nearby, artificially reducing the density of emitters. The emission plots of several cathodes are shown in Figure 4. The longer 13 micron nanotube array was driven to high field, and gave excellent emission results. After seasoning the cathode, the 13 micron emitter demonstrated current >0.3mA at 5 V/micron as shown in Fig. 5.
We have calculated parameter fits to the data, and the nanotubes have a field intensification factor near 1300, and seem to have a lower work function than graphite, near 1.8 eV.



A B

Fig. 3. Edge on views of nanotube arrays, show the variation of nanotube length.

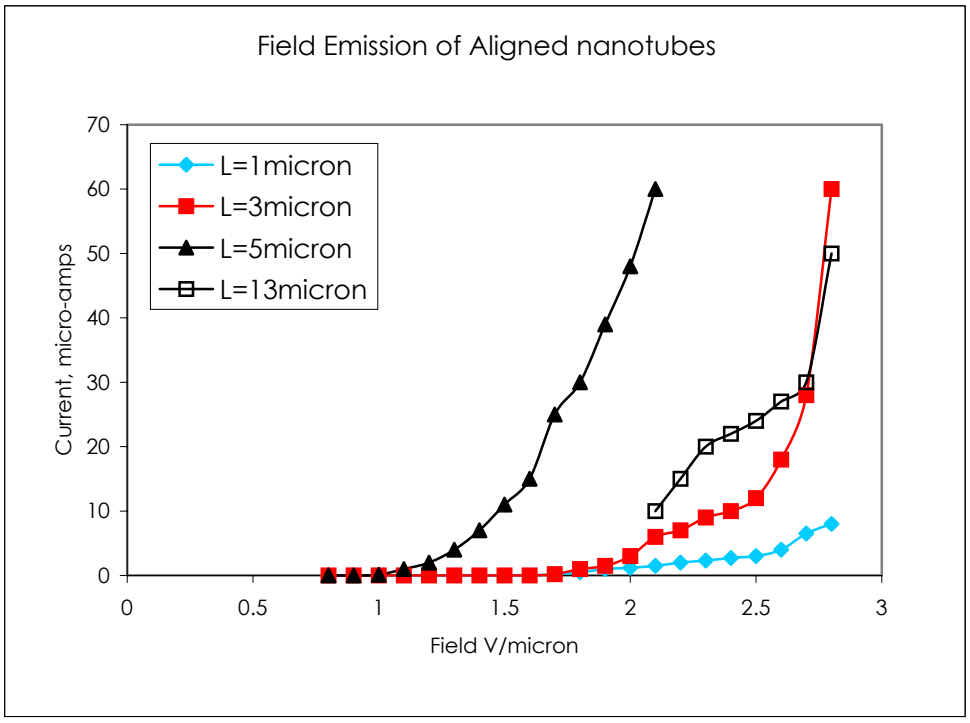


Fig 4. Short nanotube emitters have higher onset than longer ones, although the 13 micron emitter has a lower onset than the 5 micron set. All samples have 1cm2 area.

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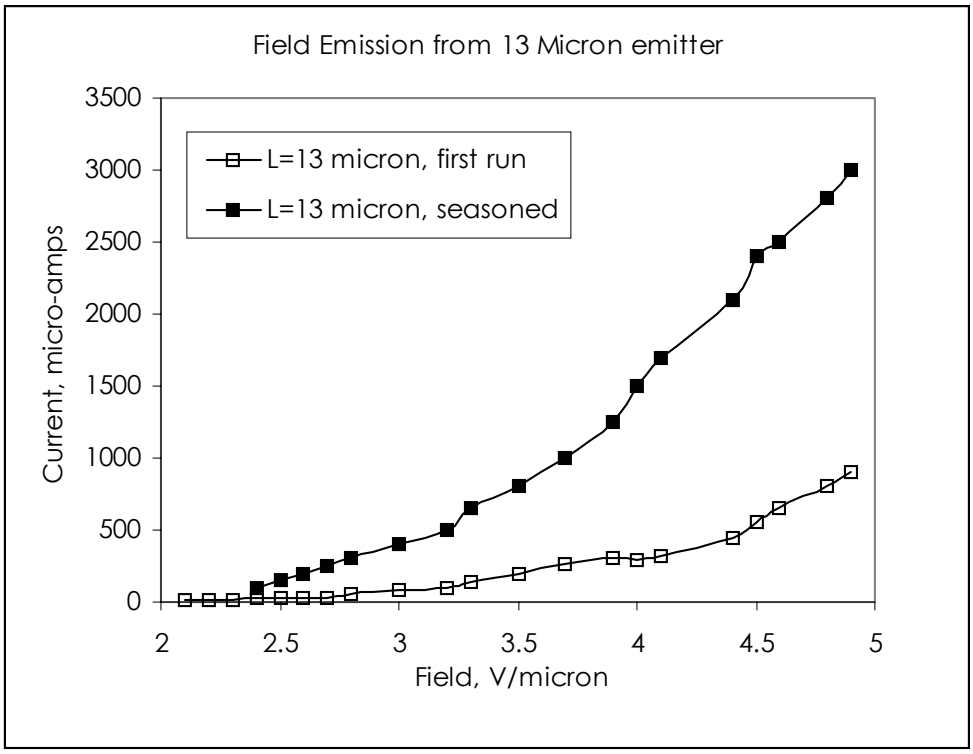

Fig 5. The 13 micron emitter became more emissive after Burn-In

Observed issues

Burn In

After running the 13 micron emitter to 1mA, and conducting a bakeout procedure, the emission characteristics improved, and the 'seasoned' cathode was driven to 4 mA.

Flickering

When imaged with a phosphor screen as the anode, areas of the cathode are seen to blink on and off. The slow timescale, multiple seconds, lead us to investigate the cause of this flicker. When the system has been sufficiently pumped and baked out, flicker is no longer observed in other nanotube systems.[2] We are developing procedures for proper bakeout and sealing to eliminate this issue.

Shielding

It is recognized that arrays of closely spaced nanotubes have lower field enhancement factors than sparse arrays, due to field shielding, as illustrated in Figure 6. The nanotube spacing distance L and the nanotube height H are critical to the field enhancement factor.

[2] Motorola Report on Carbon Nanotube Field Emission, K. Dean, MRS meeting, 2000, Boston, MA

Field Enhancement Profile

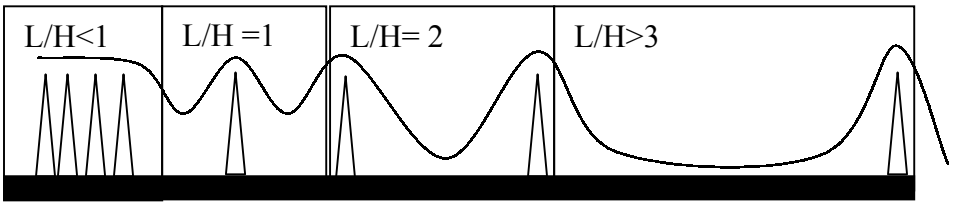

Figure 6. At ~ 2:1 L/H spacing, a dense array of nanotubes has high field enhancement.

When nanotubes are far apart, the field enhancement is strong, but the total number of emitters per unit area is low, which reduces the emitted current. When nanotubes are close together, they shield each other, reducing the field enhancement factor. At L/H ~2, an optimal spacing is reached where the field is only minimally reduced by the neighboring nanotubes, and their numbers per unit area remain high. Therefore, to produce the most effective field emission cathodes, we must create aligned, patterned arrays of nanotubes at controlled spacing.

CONCLUSIONS

The emission from aligned emitters has been demonstrated, although nanotube site densities are too high for optimal emission studies. A seasoning effect and flickering effect has been observed, both attributed to adsorbed gases on the emitter. These gases may be driven off by bakeout and burn-in. Further studies should concentrate on sparse aligned emitters to determine the enhancement of nanotube emission.

ADDENDUM

The use of a new deposition technique has allowed the production of sparse arrays of random nanotubes on substrates. This promises to create field emission arrays with more optimal site densities.

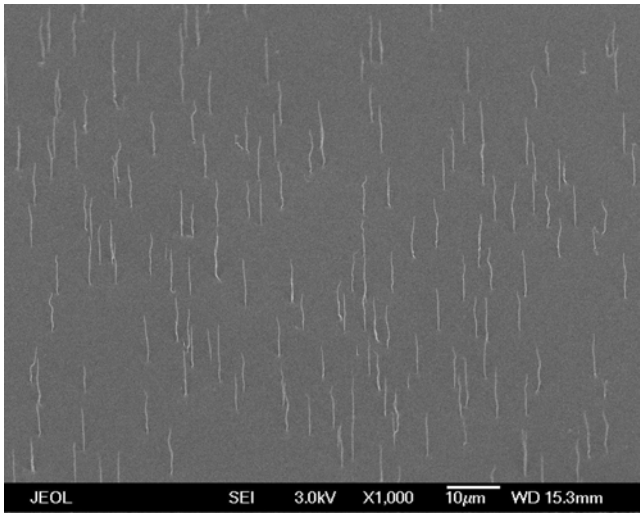

Fig. 7. Lower density nanotube arrays have been fabricated and are now being measured.

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