Heating by Field Emission from Carbon Nanotubes for Nano Manufacturing

R. R. Vallance
The George Washington University

K-F. Hii, B. Wong, P.D. Kichambare, and M.P. Mengüç,
University of Kentucky

L. Chen and S. Jin
University of California San Diego

A.M. Rao
Clemson University

K. Javed
Kentucky State University

Abstract: This paper summarizes progress in the fabrication and characterization of tools for nano manufacturing applications that employ carbon nanotubes as electron sources. Transient 3D simulations of heating suggest that electron beams supplemented with photon beams can achieve temperatures adequate for thermal evaporation and nano patterning. The tools consist of multiwall carbon nanotubes, synthesized by CVD or PE-CVD, attached to electrochemically etched tungsten tips. The field emission properties of the tips are characterized in a new calibration system that measures the current-voltage (I-V) relations as function of anode-cathode distance in the near-field. Progress in synthesizing straight and well-aligned patterns of nanotubes is also reviewed.

1. Introduction: One-dimensional nanostructures such as carbon nanotubes offer considerable advantages in precision nanomanufacturing. Various approaches for processing using 1-D nanostructures are viable, but we concentrate on applying electron beams that are readily emitted from the tips of carbon nanotubes. With high-precision computer-controlled scanning mechanisms, such as those used in scanning probe microscopy, the electron-beam can deposit highly concentrated doses of energy in the workpiece, which might be used for a variety of purposes including material removal or modification. Subsequent metrology can be conducted using the same nanotube or a second nanotube for high-resolution atomic imaging by scanning tunneling microscopy (STM) or atomic force microscopy (AFM). This approach, therefore integrates the processing and metrology into a common platform suitable for high precision nanomanufacturing.

Electrons can be emitted from a solid surface into vacuum under the action of high electrostatic fields (on the order of 3 to 6 V/nm). The field deforms the potential barrier and electrons with sufficient energy are ejected from the surface. Emitters with sharp tips benefit from magnified electric fields in the vicinity of sharp tips, so nanotubes with high aspect ratios (L/D) improve emission. Figure 1 shows a multiwall carbon nanotube with a length of about 2 µm and diameter of about 60 nm that is attached to a sharpened tungsten tip.

Fig 1: Field emitter fabricated from multiwall carbon nanotube synthesized at Clemson University and attached to etched tungsten tips at the University of Kentucky

2. Transient Nanoscale Heating by Simultaneous Electron and Photon Beams: The thermal energy transmitted from a cathode to anode during field emission of electron beams is analyzed using Monte Carlo methods that trace the trajectories of electrons and their interaction within the anode material. Using...
this approach, we determine by simulation the spatial distribution of energy deposited in the workpiece surface. Additional energy is deposited over a larger area (≈ Ø 150 nm) by a laser beam. We developed numerical techniques for simulating the energy deposition and transport within the anode workpiece due to both electron and photon beams. Descriptions of the approach and example results are available from Wong, Mengüç, and Vallance [1,2].

Fig 2 illustrates some results of these simulations in which we produce a nanoscale pattern in the shape of “UK” using a sequential pattern of “holes” from a single nanotool that is moved to twenty-one locations. The Gaussian electron beam is assumed to be 0.25 W and 4keV with a 1/e² radius of 0.25 nm. A separate 355 nm wavelength laser beam is focused to radius of 150 nm and shines through the quartz onto the bottom of the gold film.

These results suggest that the temperature can reach levels that are adequate for thermal evaporation (over 3000 K) in a nanoscale pattern if the right combination of laser and electron beam heating is applied. We are presently advancing these simulation techniques to include separate photon and electron temperatures during the transient heating.

The following sections review progress towards fabricating nanotools suitable for such heating and our experimental techniques for determining the physical limitations of the energy that can be transferred by field emission from carbon nanotubes.

3. Fabrication of MWNT Tools for Field Emission:
The nanotools consist of straight multiwall carbon nanotubes that are synthesized by chemical vapor deposition (CVD) at Clemson University or by plasma enhanced chemical vapor deposition (PE-CVD) at the University of California, San Diego. MWNTs from CVD are attached to electrochemically sharpened tungsten tips under an optical microscope [3]. This produces nanotools such as the one shown in Fig 1. The attachment is done with a micro/nano manipulator under a dark field microscope at Clemson University or under an optical microscope at the University of Kentucky.

In addition, large arrays of nanotools might be fabricated by patterning nanotubes, nanofibers, or nanocones using electron beam lithography and PE-CVD. This approach produces isolated emitters such as those shown in Fig 3. The successful growth of electron beam patterned, well-aligned, periodic array carbon nanotubes or nanocone emitter structures was recently accomplished at UC San Diego. Using electron-beam lithography, the catalyst metal was patterned into a periodic island array, which generated well aligned carbon nanotube array structure with controlled diameter and spacing during PE-CVD deposition. An applied electric field ensures that the structures grow perpendicular to the substrate surface.
Fig 3: Aligned carbon nanotubes grown at UC San Diego with plasma enhanced chemical vapor deposition in an electric field after patterning catalyst with electron beam lithography.

4. Characterization of Field Emitters: As suggested by prior reports on the field emission from carbon nanotubes [4,5,6,7], the dependence of the emitted current density on the gap distance and applied voltage is satisfactorily modeled by the planar Fowler Nordheim (FN) equation with image charge potential correction. The FN equation is given in Eq. (1), where, \( \phi \) and \( E \) are the work function in eV and local electric field in V/m, respectively. The constants \( B \), \( C \), and \( D \) are \( 1.5 \times 10^{-6} \text{ AeV}^2 \), \( 10.4 \text{ eV}^{0.5} \), and \( 6.44 \times 10^9 \text{ VeV}^{-1.5} \text{m}^{-1} \), respectively.

\[
J = B \frac{E^2}{\phi} \exp \left( \frac{C}{\sqrt{\phi}} - \frac{D\phi^{1.5}}{E} \right)
\]  

(1)

The FN equation can be converted into experimentally measurable quantities by rewriting Eq. (1) in terms of the emitted current and the applied voltage. This is accomplished by assuming that the current density equals the ratio of current to an effective emitting area \( J = I/A \) and that the local electric field equals the product of the field enhancement factor \( \beta \) and the macro field \( E = \beta V/d \). These substitutions yield the emitted current in Eq. (2), where, \( A \), \( V \), \( d \), and \( \beta \) are emitting area in \( \text{m}^2 \), applied voltage in V, anode-cathode gap in m, and the field enhancement factor, respectively.

\[
I = A \frac{B}{\phi} \left( \frac{V}{d} \right)^2 \beta^2 \exp \left( \frac{C}{\sqrt{\phi}} - \frac{D\phi^{1.5}d}{V} \right)
\]  

(2)

Since the work function \( \phi \) is typically 4.8 to 5.0 eV for carbon nanotubes, the effective emitting area and field enhancement factor can be determined by experimentally fitting measured I-V data to Eq. (2).

Initial experiments to measure I-V relations for a nanotool, such as the one shown in Fig. 1, were conducted at UC San Diego. The MWNT was synthesized at Clemson University and attached to sharp tungsten tips at the University of Kentucky. Fig 4 shows a photograph of the setup to measure current-voltage (I-V) curves. The emission current for a single nanotube attached to the end of tungsten tip was measured to be ~1 microampere at a voltage of ~450 V, giving rise to a significant power level of 0.45 mW from the emission. The 1 microamp for the carbon nanotube diameter of ~25 nm is equivalent to a current density of more than 100,000 amperes/cm². The log(I/V²) vs 1/V plot indicates the typical Fowler-Nordheim relationship.

![Tungsten Tip (with an attached nanotube cathode)](image)

Fig 4: Experiment conducted at UC San Diego to measure field emission from a single nanotube attached to a sharp tungsten tip.

The University of Kentucky recently completed and demonstrated another technique for calibrating the emitters as functions of voltage and anode-cathode distance. Their technique uses the apparatus illustrated in Fig. 5, which consists of a nanopositioning stage, a high gain current amplifier, and a low-noise low-current-leakage high voltage power supply. Experiments are controlled with a personal computer that records measured data. The nanopositioning stage is guided by a double-compound flexural bearing [3] that is actuated by a UHV-compatible piezoelectric actuator with 20 \( \mu \text{m} \) displacement range. The anode and cathode are passively aligned when they are pushed into two grooves that are micromachined in quartz substrates [8]. The anode remains stationary, and the cathode displaces when the piezo actuator presses against the flexural bearing. Stainless steel wires preload the electrodes into the grooves and provide electrical contact to the anode and cathode.

The cathode (CNT emitter), as illustrated in the Fig. 5, is an etched tungsten wire (150 \( \mu \text{m} \) in diameter) with an individual CNT (~ \( \emptyset \) 60 nm x 2.1 \( \mu \text{m} \) in length protruding away from the W tip) attached to its tip and the anode is an optical fiber (125 \( \mu \text{m} \) in diameter) coated with Cu layer along its radial direction serving as an electrically conductive medium to the Au coated layer on the end face. The current amplifier used to

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measure the emitted current from the field emitter is a variable gain setting (10^3 to 10^11 V/A) Keithley current amplifier (Model 428). And, the high voltage power supply is the Model 230-03R from Bertan with remote control utility. In the field emission measurements of this work, the cathode is at a voltage potential close to the ground potential (may vary) and the anode is at a positive voltage potential. All field emission measurements are performed under a vacuum base pressure of about 4.0 × 10^{-8} mbar (3.0 × 10^{-8} Torr).

The I-V characteristics of a nanotool at five different gap distances, d = 2.0, 2.5, 5.5, 9.0, and 13.5 µm, are illustrated in Fig 6. For emission currents below 0.2 µA, the emitted current is well modeled by FN theory. And, this observation is further supported by a FN plot of the experimental I-V data (not reproduced here) that exhibits the well-known straight-line behavior. The I-V characteristics of the CNT field emitter are found to be strongly dependent on the electrode gap distances. The changes in the I-V characteristic are even more noticeable for gap distances below 2.5 µm (i.e. notice the “shift” in the I-V curves at d = 2.0 and 2.5 µm with only 0.5 µm changes in the gap distance). For emission currents above 0.2 µA, a “saturation” in emission current is observed, and I-V curves depart from FN model.

The turn-on voltage is strongly dependent upon the electrode gap distance as illustrated in Fig. 7. The turn-on voltage, \( V_{to} \), decreases from about 75 V to 48 V as the gap distance decreases from 13.5 µm to 2.0 µm. The empirical relationship between the turn-on voltage and the gap distance (unit used here is in µm) from the least-square best-fit curve to the experimental data is approximately \( V_{to} = 41.2d^{0.21} \). A power function is chosen for its behavior that is more analogous to tunneling behavior in STMs (typically < 10 V and gaps < a few nanometers) rather than a best-fit line that intercepted the ordinate at a turn-on voltage of 47 V.

The field enhancement factor is also found to depend strongly on the electrode gap distance as illustrated in Fig. 7. The field enhancement factor decreases from 852 to 174 with decreasing gap distance. In theory, the field enhancement factor is the enhancement in the external electric field at the apex of an emitter due to the devices geometry (geometry of electrodes and their separation). This factor is independent of the applied voltage for a given electrodes gap but dependent on the gap distance due to the changes in the electric field lines (vectors). The empirical relationship between the field enhancement factor and the gap distance (unit in µm) from the best-fit curve to the experimental data is \( \beta = 2036 \frac{d}{(d+25)} \); this curve shape is selected based on Miller’s work [9]. The constants in the curve-fit suggest a field enhancement factor of 2036 at an...
infinite distance and an effective emitter length of 25 µm, which is longer than the MWNT but incorporates the affect of the sharpened W tip.

Fig 7: Dependence of turn-on voltage and field enhancement factor on anode-cathode distance

The effective emitting area was observed to be independent of the gap distance (as expected from theory) and ranged from 3.0 to 310 nm². If a circular effective emitting area is assumed at the apex of the CNT, then the radius of the circular area ranged from 1 to 10 nm, which is smaller than the MWNT radius of about 30 nm. It should be recognized, however, that these effective emitting areas are determined from the planar FN theory which doesn’t account for (a) the emitter’s surface not being planar (b) the local electric field and current density are not constant over the emitter’s surface, and (c) the FN J-E relationship is not proportional to the experimental I-V due the dependency of the emitting area on the electric fields at the apex.

At UC San Diego, experiments are being conducted to characterize the patterned arrays of emitters such as those shown in Fig 8. As shown in the data of Fig 8, these arrays are capable of producing higher currents since multiple MWNTs emit simultaneously. The emission current density for the aligned nanotube array (Fig. 8) is very high, ~3.8 A/cm².

Fig 8: Emission I-V curves for nanotube array.

6. Conclusion: As conductive 1D nanostructures, carbon nanotubes are well suited for precision nanomanufacturing applications. Thermal energy in the form of an electron beam can be transferred from the cathode to anode, and numerical techniques for simulating this heating are being developed. Techniques for synthesizing the MWNTs and preparing nanotools with MWNTs continue to be developed, especially for large arrays of emitters. A new technique was described for calibrating the near-field field emission from nanotools with individual nanotubes. The method enables the determination of field enhancement factors and turn-on voltages as functions of the gap distance (below 20 µm).

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10. References: