Preparation of a carbon nanotube field emitter and deduction of its properties from the Fowler-Nordheim plot

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Abstract. We describe the preparation of a carbon nanotube for field emission measurements, and deductions from its measured current-voltage characteristic. The slope of the Fowler-Nordheim (F-N) plot is not constant but increases slightly in magnitude as the anode-cathode voltage $V_a$ is reduced. By modifying F-N theory for emission from a hemispherical surface, and using the rate of change of slope, it is possible to deduce the radius of curvature of the emitting region, surface field, effective solid angle of emission and an electron supply factor, more precisely than is feasible using planar theory.

1. Introduction
Attempts to deduce the properties of field emitters from measurements of emitted current as a function of anode-cathode voltage have often been made using the established theory of field emission [1]. It has usually been difficult to obtain values of parameters that are both consistent and realistic, partly because of the difficulty of measurement on the emitter, but also because the well-known theory still relies on the initial approximation that the field outside the emitter is uniform, as if the emitting surface and anode were planar.

We have obtained more precise results from the measured characteristic by assuming a more realistic distribution of potential outside a curved emitter. The calculation of current then suggests that the Fowler-Nordheim (F-N) plot has a slight curvature, which increases with the curvature of the emitting surface. If this feature of the F-N plot can be measured sufficiently accurately, it can be used to determine parameters of the emission. Recently, measurements have been made on a carbon nanotube which has been carefully cleaned, resulting in a smooth and slightly curved F-N plot. The deductions that have been made from this plot include an estimate (not available using the conventional theory) of the electron supply at the real emitter’s surface relative to that calculated for a free-electron metal.

2. Preparation of nanotubes
To enable measurement of electron emission, an individual carbon nanotube (CNT) was mounted on a tungsten support tip connected to a heating filament. The mounting procedure was performed in a scanning electron microscope (SEM) equipped with a nano-manipulator. A tungsten tip was first pierced into carbon tape to apply glue necessary for a firm attachment of the nanotube. A sample with nanotubes protruding from a sharp edge also placed in the SEM was searched for a long, straight, thin and freestanding nanotube. This nanotube was brought into contact with the tungsten tip, on which it...
stuck (see Figure 1). Then the nanotube was broken off the nanotube sample by applying a voltage difference over the nanotube. For optimal use as electron source, CNTs with open caps are unwanted, as the manifold of dangling bonds from an open cap lead to current fluctuations and may even lead to a quick destruction of the nanotube under the presence of the extremely strong electric field needed for electron emission. Therefore, the caps were closed after the mounting by a closing procedure. The closure occurred for carbon nanotubes with up to 5 walls upon emission of a current of a few microamperes [2]. The final step in the preparation of the CNT electron source was cleaning. A newly-made electron source was transferred into an ultra-high vacuum system (10^{-10} Torr) for the characterization of the electron emission properties. The nanotube was heated first to the carbonization temperature of 700 ± 50º C for 10 minutes to remove volatile species from the tube. The samples were heated to a temperature of 300º - 500º C during the emission experiments to continuously clean the tubes. Field emission microscopy (FEM) was used to investigate the tube caps of the carbon nanotubes. FEM images provide information on the electronic structure and the local tunnelling probability of an emitting area. The emission patterns of carbon nanotubes with closed caps were almost round and had several local maxima within the emission pattern, but with no sharp transitions from regions of low to high intensity. These patterns were highly stable with time for emitted currents up to 1 µA as expected for a closed cap.

Figure 1 Method of mounting a CNT electron source as performed inside a scanning electron microscope. (a) A CNT protruding from a thin substrate containing many nanotubes is selected and (b) attached to a tungsten support tip. (c) The nanotube is broken by Joule heating. (d) The open tube end is finally closed.

3. Electrical measurements
The current-voltage measurements on a single CNT mounted as above have been reported previously [3]. In that report the experimental points on a F-N plot were fitted by a straight line, for the purpose of applying standard F-N theory. Figure 2 shows a plot of the same points fitted by a quadratic function so as to determine the variation of slope with applied voltage.

Fig. 2  F-N plot for ‘nanotube 1’ reported in [2], with quadratic fit.
4. Potential model

Details of the theory for emission from a hemispherical surface are given elsewhere [4]. The potential distribution in the barrier region around a hemispherical surface has been modelled by the following analytic approximation to the computed potential near a hemisphere on a cylinder:

\[ V(R, \theta) - E_f = \phi \left[ 1 - \left( R^{1/2} - R^{-3/2} / 2 \right) \right] / \kappa / \left( R^2 - 1 \right) \]

where \( \phi \) is the work function of the surface, \( x(\theta) = \phi / a e F(\theta) \) [\( = \kappa F_{\text{max}} / F \)], \( R = r / a \), \( \kappa = e^2 / 4\pi\epsilon_0 \phi a \) [\( \approx 1.44 \text{ eV nm} / \phi a \)], \( a \) is the radius of curvature of the emitting surface, \( r \) is the radial co-ordinate from the centre of curvature, \( -e \) is the charge on the electron, \( -F \) is the electric field at the surface and \( -F_{\text{max}} \) is the field at which the top of the potential barrier is reduced to the Fermi level (\( \approx 17.4 \text{ Vnm}^{-1} \) for \( \phi = 5 \text{ eV} \)). \( F(\theta) \) has been computed and is assumed here to vary as \( \cos(\theta / 2) \), where \( \theta \) is the angle from the axis of the emitter. It is convenient also to define two dimensionless functions of the barrier potential distribution, \( f_1 \) and \( w_1 \), which can be expressed as functions of \( \kappa \) and \( x \)

(figures 3, 4). From the known variation of field over the emitting surface, an effective solid angle of emission \( \Omega \) can be determined. The ratio of observed current \( I_{\exp} \) to that calculated for a free-electron emitter is defined as \( \sigma \). The resulting expression for \( I_{\exp} \) is then

\[ I_{\exp} = \left( \frac{\sigma \Omega b_1}{w_{10} x_0^2} \right) \exp \left[ -b_2 f_{10} / \kappa \right] \]

where \( b_1 = \phi e / 8\pi h \), \( b_2 = 2 e^2 (2m)^{1/2} / 3 e_0 \vartheta^2 h \), and the subscript \( (0) \) to \( f_1, w_1, \text{and } x \) denotes values on the axis.

5. Slope of F-N plot

An expression for the slope of the F-N plot, \( S_x \), can be found from (1) and related to \( df_1 / dx \). The resulting equation can be solved iteratively for \( \kappa \) when \( S_x \), \( V_e \) and an arbitrary value for \( x \) are given. If the slope is known at only a single value of \( V_e \), then solutions can be found for a range of pairs of values of \( x \) and \( \kappa \). For each of these pairs, we can calculate \( dS/dV_e^{-1} \) at the same \( V_e \). The magnitude of this rate of change increases steadily with \( \kappa \) (Fig. 5). Hence, if \( dS/dV_e^{-1} \) can also be found experimentally, then we can find one pair of \( \kappa \) and \( x \) at which these rates of change match. It is then possible to find the corresponding values of all other variables, including the supply factor \( \sigma \).

6. Deductions

When this procedure is carried out using the measurements of Fig. 1 and with \( \phi \) assumed to be 5 eV, we find:
Radius of the emitting region, \( a \): 1.24 nm  
Field strength \( F \) on axis at \( V_a = 625 \) V: 11.3 Vnm\(^{-1}\)  
Effective solid angle, \( \Omega \): 1.54 sr  
Supply factor relative to free-electron metal, \( \sigma \): 0.135

The plot of \( \sigma \) as a function of \( x \) and \( \kappa \) in figure 6 shows that an assumption made in the theory, that \( \sigma \) is independent of \( V_a \) (and \( x \)), is satisfied only at the same value of \( \kappa \) as was found from figure 5. This appears to offer a second way of determining \( \kappa \).

Fig. 5. \( dS/dV_a^{-1} \) for nanotube 1 as function of \( \kappa \). The experimental value is obtained with \( \kappa = 0.233 \).

Fig. 6. Calculated \( \sigma(\kappa, x) \). At \( \kappa = 0.233 \), \( \sigma \) is independent of \( x \) and \( V_a \).

7. Conclusion
The hemispherical theory provides a physically realistic model of the variation of field and current density over the emitting surface. It also shows how the slope of the F-N plot can be expected to vary with \( V_a \) and with the radius of curvature of the emitting surface. Where only a single value of slope is known, then a range of values of emitter radius and other parameters can be found. When the rate of change of the F-N slope can be found from experimental measurements, the hemispherical theory enables a single set of parameters to be determined. In addition, it offers a new way of measuring the electron supply factor of the emitter.

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