A simple and robust electron beam source from carbon nanotubes

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A simple fabrication method is described to produce reliable and robust (self-repairing) field emission sources from randomly aligned carbon nanotubes. The sources display stable and reproducible current–voltage characteristics with sharp turn on near 100 V and emission currents up to 400 mA/cm^2 at 200 V. Two successful methods are described for patterning the emission source area into emitting and nonemitting regions. © *1996 American Institute of Physics.* [S0003-6951(96)04039-9]

Carbon nanotubes[1] have interesting structural and electronic properties which suggest a host of useful applications ranging from high-strength, lightweight fibers to chemical filters and catalysis aids to miniature electronic wires and devices. All nanotubes feature high aspect ratios and small radii of curvature at their tips, characteristics particularly advantageous for electron field emission. Indeed, Rinzler *et al.*[2] have demonstrated laser-irradiation-induced electron field emission from an individual carbon nanotube, and de Heer *et al.*[3] have used arrays of carefully aligned carbon nanotubes to produce field emission sources.

In this communication, we confirm nonlaser-assisted nanotube field emission and describe a new carbon nanotube random-matrix fabrication process resulting in a stable, high-density electron beam field emission source. The source is ''self-repairing'' and thus virtually impervious to mechanical or electrical damage. Unlike previous configurations, alignment and manipulation of the nanotubes in the random matrix process are completely unnecessary, making large scale fabrication straightforward and exceedingly simple.

Carbon nanotubes were synthesized in a conventional plasma arc-discharge[4] as described elsewhere.[5] The tubes were dispersed in ethanol and burned in oxygen to remove amorphous and graphic carbon particles,[6] then characterized by transmission electron microscopy (TEM). The tube-rich material was observed to be composed of at least 70% multiwalled tubes with diameters between 5 and 50 nm and lengths up to 10 μm. High resolution TEM inspection of the tubes ends are tapered, with ultimate tip radii of curvature smaller than the distribution of tube diameters would suggest. The sharpest tips, which are most likely to act as emitters, were observed to have radii of curvature between 1 and 3 nm. Thus, in a random collection of tubes of different diameters, it is possible that a large fraction of the tubes serve as efficient electron emitters, with emission properties only weakly sensitive to the distribution of gross tube geometric or electronic properties.

The tube-rich material was mixed into nonconducting epoxies in volume ratios of approximately 1:1, resulting in solidified conductive mixtures with typical resistivities ~500 Ω cm. No attempt was made to align the nanotubes within the epoxy matrix; rather, they are assumed to be completely disordered. A small fraction of the tubes pierce the epoxy surface and extend their tips outward well beyond the surface. It is these extended tubes that constitute the emission source of the sample surface.

For the experiments described below, a fixed 50 μm×50 μm emission surface area was prepared by drying the epoxy-nanotube matrix under pressure between glass slides spaced 50 μm apart and grinding down the resulting edge. The emission surface was then lightly polished to ensure a reproducible and macroscopicallay flat surface. Scanning electron microscopy (SEM) characterization of the polished surface resolved bundles of nanotubes tubes on the surface, with a typical density of 1 bundle per μm^2, sticking out in all directions like the spines on a cactus. Figure 1 shows a typical SEM image of the emission surface, as well as a depiction of the sample geometry. The clearly imaged tubes indicate that the bases of the nanotubes remain firmly embedded in the conductive epoxy matrix, to which electrical contact is made.

The samples were attached to a flexible holder in vacuum and aligned directly above a 3 mm diameter conducting grid, then placed in a vacuum chamber at 10^{-6} Torr. A micrometer allowed variation of the grid-sample separation, which we define from the epoxy surface and not the extended nanotube tips. Negative dc voltages up to 1000 V were applied to the sample, and the emission currents which passed through the 50% transmitting grid were collected and measured by an electrometer.

Figure 2 shows a typical emission current (I) versus
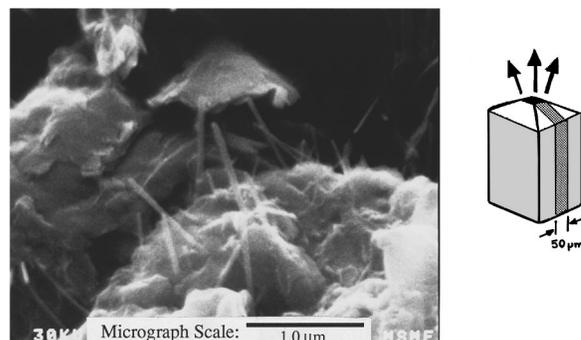
FIG. 1. SEM micrograph of the nanotube matrix emission surface. Tube bundles can be seen bristling from the matrix surface with an approximate density of 1/μm^2. The sketch on the right depicts the matrix sample laminated between glass plates. The emission facet on top has an area of 50 μm×50 μm.

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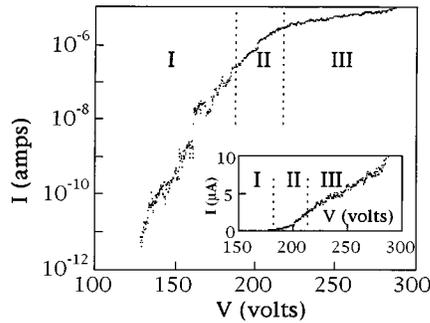
FIG. 2. *I–V* curve for field emission from carbon nanotube matrix sample on a log-linear scale. The inset shows the same data on a linear-linear scale. Three distinct emission regions (I, II, and III) are observed.

sample-to-grid bias voltage (*V*) characteristic on a log-*I*, linear-*V* scale. The current displays a sharp onset near 130 V and increases exponentially with increasing *V*. Distinct regions are easily identified. Below the onset voltage, the device is ''off'' with currents below our experiment limit of 1 pA. Above the onset, the emission turns on but increases at different rates in three voltage regions, as labeled in the figure. In region I, the current rises exponentially at a rate of 1 order of magnitude every 10 V up to a current of 10 nA. In this region, the emission current has $\pm 50\%$ fluctuations, as well as short-lived current decreases by an order of magnitude. The exponential rise rolls off in region II, and the negative curvature in the log-*I* representation indicates tendency towards some type of current saturation. In region III, at still higher voltages, the current again rises exponentially but at only one-tenth the rate of region I. The inset to Fig. 2 shows the same data plotted on a linear-*I*, linear-*V* scale.

Under constant voltage bias in region III, the samples display stable emission currents over many hours. At a bias of 200 V, total emission currents ranged from 0.01–10 μA depending on the initial density of tubes used in the matrix preparation. For our sample size, this corresponds to current densities as high as 400 mA/cm². Assuming that every tube observable in an SEM image emits, each tube must on average carry 10 nA. It is possible that only a small fraction of the tubes actually emit and those that do carry much higher currents.

Conventional field emission analysis utilizes the Fowler–Nordheim equation.[7] The effective local electric field E_{loc} at an emitting tip determines the emission current density at the tip surface $J \propto E_{\text{loc}}^2 \exp[-7 \times 10^7 \Phi^{3/2}/E_{\text{loc}}]$, where Φ is the local work function of the emission tip. In the matrix sample configuration studied here, the total emission current may be due to an ensemble of emitting nanotubes, for which the Fowler–Nordheim equation is not directly applicable. However, assuming a narrow distribution of emission parameters, it provides a first order characterization of tube emission properties.

First, the local field E_{loc} must be determined. With a sample-grid separation $d = 20$ μm, the observed bias onset voltages for field emission are approximately 100 V, corresponding to an average applied electric field $E_{\text{avg}} = 5 \times 10^4$ V/cm between the sample surface and the grid. However, we observe only small deviations in the onset voltage as d is

varied from 20 to 100 μm, with otherwise identical *I–V* characteristics. This independence, as well as the relatively small value of E_{avg}, suggests that the actual local field at the nanotube tips is not simply the voltage bias per separation *nor proportional to it*. Practically, the independence of the emission current on *d* is of tremendous importance as it allows large fabrication tolerances. Physically, it suggests that the electric field is indeed confined to the immediate region of the tip by a high concentration of charge.

For an emission current insensitive to the sample-grid separation, as we observe, the nanotube tips may be modelled as nearly isolated, charged hemispheres.[8] Then the local field depends only on the applied bias V yielding $E_{\text{loc}} = V/\alpha R_{\text{tip}}$, with α a constant of order unity. For our known tip radius of ~ 2 nm and a value of $\alpha = 3$, we calculate a local field $E_{\text{loc}} = 2 \times 10^8$ V/cm. Although nearly 10 times higher than the onset field for metallic emitters, this value is reasonable considering the possible semiconducting nature of the carbon nanotubes.

Having determined the local field, we may determine the tip work function from the exponential behavior of the *I–V* curve. By the usual technique of plotting $\text{Ln}(I/V^2)$ vs $1/V$, we obtain straight lines in region I and region III with slopes of 2500 and 450, respectively. These suggest tip work functions of 13 eV in region I and 4.2 eV in region III. For comparison, graphite has a work function of 5 eV. We draw the preliminary conclusion that only region III is truly in a Fowler–Nordheim regime. The anomalously sharp turn on in region I is interesting both theoretically and from the point of view of practical applications.

Although the emission onset voltage shows some sample-to-sample variation, all of our prepared samples show the same three-region characteristic *I–V* structure depicted in Fig. 2 and emission currents of at least 1 nA at 200 V. Handling of the samples notably does not affect the field emission density or stability. Samples were routinely brought into direct contact with the grid to calibrate the separation distance, with no change in field emission quality or character. To further test sample robustness, samples were arced at high voltage against the grid, momentarily passing up to 100 mA of current. Despite the likelihood of significant surface damage, emission from arced samples exhibited similar voltage onsets and current magnitudes. The persistence of emission is due to two factors: (1) the density of tube tips is uniform throughout the epoxy matrix, so that removal of surface material creates as many emitters as it destroys, and (2) the emission character only weakly depends on the grid separation, so tube tips on a textured surface emit as well as they do from a smooth surface. Thus, the emission surface is not sensitive to individual tubes breaking, bending, or otherwise being damaged. Instead, the surface is self-repairing in terms of its emissive properties.

We have also investigated two means of patterning our samples into emitting and nonemitting regions, as might be necessary for independently controlled emitters. A metal (e.g., gold) overlayer as thin as 5 nm screens the nanotube tips from high electric fields and quenches all field emission. No current was detected at biases up to 1000 V from gold-patterned samples which previously had emitted. In a second method, ion sputter etching of the sample was used to dam-

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age the surface and emitting tips. Samples were bombarded with Ar^+/fluxes of 15 mA for up to 10 min. Field emission persists in samples exposed to the maximum dosage, although with significant degradation. The voltage onset is raised 50 to 75 V, and the transition from region I to region III occurs at a reduced current of 1 nA instead of 10 nA. At a particular bias, the emission from the sputtered sample is also much less stable over time. The sputtered samples do not have any ''on'' regions at which they emit stably over time.

The sputter etching, though not as effective as the metal overlayer at eliminating emission, may nevertheless be the more important technique for device fabrication. Focused ion damage could produce non emitting regions without the shielding effects to be expected from metallic separations.

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