Field electron emission from individual carbon nanotubes of a vertically aligned array

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Field electron emission behavior of individual multiwalled carbon nanotubes (MWNTs), that are elements of a vertically aligned array grown on a Si wafer, were analyzed with a scanning anode field emission microscope. The electron emission of each MWNT followed the conventional Fowler–Nordheim field emission mechanism after their apexes were freed from the erratic adsortion species using a conditioning process at room temperature. The conditioning process led to stable emission currents and reduced their variations $\Delta I/I$ to less than 30% between different MWNTs of the array. This opens the possibility for using MWNTs in an array as independent electron sources for massively parallel microguns. © 2002 American Institute of Physics.

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The aim of this article is to assess the suitability of multiwalled carbon nanotubes (MWNTs) arrays, grown by plasma-enhanced chemical vapor deposition (PECVD), as field emission (FE) cold cathodes for an “on-chip” arrayed microguns. These arrays may then be used for massively parallel electron lithography. As each of these microguns are to be used as independent electron columns, we need to answer the two following questions:

1. Can the emission characteristics from a single MWNT be made stable and reproducible? Answering this allows us to determine what is required to obtain reproducible emission behavior from a single MWNT emitter.

2. What is the variation of the emission current between different MWNTs within a vertically aligned array of nanotubes obtained from the same fabrication process? The adoption of MWNTs as electron sources for on-chip arrayed microguns is only possible if the variation between nanotube emitters is small and the nanotube emitters can be fabricated with a yield near 100%.

Electron emission studies of carbon nanotubes, in particular for those deposited on a planar surface, encounter the two following main difficulties, compared to conventional metallic tips in FE studies. Namely, it is not possible to clean the surface by controlled thermal treatments at high temperatures, and it is difficult to determine the exact geometry of the actual emitter during the emission unless the emission is from an isolated, individual nanotube. In experiments in which the nanotubes can interact with each other (e.g., in a “forest” of nanotubes), there is a great uncertainty in the exact determination of the geometrical $\beta$ factor which converts the applied voltage $V_{\text{app}}$ to the local field at the apex, $F_{\text{local}} = \beta \times V_{\text{app}}$, which acts in the tunneling process to extract the electrons from the surface. Because of this uncertainty, it is very difficult to find a correlation or to even agree upon a common emission mechanism using the experimental data in the literature for field emission from ‘forests’ of nanotubes.

In this letter, scanning anode field emission microscope (SAFEM) [Fig. 1(a)] analyses were performed on individual vertically aligned MWNTs of an array grown on a Si wafer by a dc PECVD at $\sim$700 °C using a C$_2$H$_2$ and NH$_3$ gas mixture with Ni catalyst. The growth process is described in detail elsewhere. In order to achieve the growth of an individual nanotube, high resolution electron beam lithography was used to pattern the Ni catalyst. The voltage drop in the plasma sheath during PECVD generates an electric field perpendicular to the surface, and this causes the nanotubes to align vertically on the substrate during growth. The sample used for this study was an array of 40 $\times$ 40 individual MWNTs ($\sim$5 $\mu$m tall and $\sim$60 nm in diameter) at a spacing of 100 $\mu$m. Figure 1(b) shows a similar array with smaller spacing (10 $\mu$m). The value of 100 $\mu$m for the spacing is chosen to ensure that individual nanotubes were probed during SAFEM analyses. The diameter of the scanning Pt–Ir probe tip is 30 $\mu$m.

FIG. 1. (a) Schematic drawing of the SAFEM set up. (b) SEM observation of a vertically aligned array of MWNT ($\sim$5 $\mu$m tall) with a spacing of 10 $\mu$m. In this photograph the spacing is 10 $\mu$m in order to have on the same photo the array and the MWNTs.

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determine an appropriate procedure based on FE in order to obtain reproducible and the probe-ball measurements strictly followed the conventional Fowler– Nordheim (F–N) equation, i.e., plotting \( \ln(I/V^2) \) versus \( 1/V_{\text{app}} \) resulted in a straight line [Fig. 2(a), plot 3]. (3) After conversion of \( (I-V_{\text{app}}) \) into \( (I-F_{\text{local}}) \), \( \phi \) was determined from F–N plot giving a value of \( \phi \approx 4 \) eV. (4) For \( I_{\text{FE}} \approx \) few \( \mu \)A, the emissions were very stable, with fluctuations \( \Delta I/I \approx 10\% \) [Fig. 2(b)]. This means that the adsorption on the MWNT apex during the emission was negligible even within a vacuum between \( 10^{-8} \) to \( 10^{-9} \) Torr. (5) After a long period without emission in vacuum, the FE characteristics of the MWNTs changed, but a recovery to the same F–N plot was obtained after a conditioning process. This means that the conditioning process generally led to the same status of the surface at the apex.

Before the conditioning process, i.e., using the nanotube sample in the as-growth condition, we found that (1) The emission onset/threshold \( V_{\text{app}} \) to obtain \( 1 \) pA was two to three times less than after the conditioning process. (2) The FE currents were very unstable with high fluctuation rate [Fig. 2(c)]. (3) The \( (I-V) \) characteristics always exhibited current saturation [Fig. 2(a) plot 1], a behavior which was also observed by other authors, and these plots were not reproducible. This means that irreversible modifications of the surface occurred during the emission.

The room temperature conditioning process we used is the following three-step procedure: (1) Just after the start of emission (1 pA), the emission current is steadily increased until a sudden decrease in the current is observed. This sharp drop in \( I_{\text{FE}} \) generally occurred when it reached \( \sim 0.1 \) \( \mu \)A. (2) After this sharp decrease, the \( (I-V) \) plots which showed saturation [Fig. 2(a), plot 1] evolved towards a straight line as the maximum conditioning currents were increased gradually from 0.1 \( \mu \)A to a few \( \mu \)A [Fig. 2(a), evolution from plot 1 to plot 2]. Concurrently, there was a noticeable decrease in both the occurrence and amplitude of the observed fluctuations in the emission current \( (\Delta I/I) \) at fixed \( V_{\text{app}} \). (3) Thereafter, by increasing the conditioning current to 5 \( \mu \)A or more, reproducible straight lines for the F–N plots [Fig. 2(a), plot 3] with very stable emission current [Fig. 2(b)] were obtained.

We interpret the conditioning process as a cleaning of the surface at the apex of the MWNT. Just after the introduction of the sample into vacuum, surface adsorbates were always present at the apex of the MWNT, this is a very well known phenomena observed for various types of tips using field emission microscopy. FE with an adsorbate-covered apex begins at small localized areas that have the smallest work function. This causes the rapid formation of nanoprotrusions due to electric field-driven surface diffusion of the adsorbates. From the measurement point of view, this corresponds to the observed instabilities and large fluctuation rate in the emission current. At these protrusions, local heating by Nottingham effect occurs, causing an increase in the local temperature as a function of the current. The local increase in temperature was possibly enhanced by Joule heating along the MWNT. At large current densities, the local temperature becomes high enough to field evaporate some of the adsorbates, and consequently an increase of the global work function at the apex occurs. From the measurement point of view, this corresponds to the observed evolution (i.e., nonreversible/shifting) of the \( I-V \) plots with initially current saturation. After \( I_{\text{FE}} \approx 5 \) \( \mu \)A, most of the adsorbates were removed, and the FE generally occurred when it reached \( \sim 0.1 \) \( \mu \)A.
field evaporated and those that remained were strongly bonded to the surface. From the measurements point of view, this corresponds to a stable emission with reversible F–N characteristics, with $\phi \approx 4$ eV.

So far, we have shown that the proposed conditioning process leads to reproducible FE characteristics for a single MWNT. The following observations deal with the variation of FE characteristics between each vertically aligned MWNT in an array grown simultaneously on the same substrate: (1) Before the conditioning process, the first constant-voltage scan at a fixed distance over the array yielded large differences in the emission currents from one MWNT to its neighbors. In some instances, the variation in emission current between emitters was 1000. (2) Nevertheless, for all the scanning measurements performed for this study (i.e., three lines having six aligned MWNTs and two matrices of 3 $\times$ 3 MWNTs), emission currents have been observed from all the nanotubes in their expected positions. This implies that the 100% yield in the fabrication of the MWNT array, as shown in Figure 1(b), was obtained also for field emission. (3) After the conditioning process, most of the MWNTs exhibited very similar emission characteristics. Figure 3(a) shows the current variation over four MWNTs located at the corners of a 100 $\mu$m square array, with their corresponding F–N plots in Fig. 3(b). For this array, $\Delta I/I \lesssim 30\%$ for a same applied voltage and the values for $\phi$ obtained were 3.90, 4.12, 4.21, and 4.04 eV respectively. Such a similar $\phi$ between emitters suggest that the apex of the different MWNTs were mostly identical after the seasoning process. This could be possible since the same geometry of the nanotubes obtained by PECVD were almost identical [Fig. 3(c)], i.e., the same apex radius. Furthermore, the graphitic nature of the surface at the apex favors physical adsorption, and so the field evaporation of the adsorbates during the seasoning process leaves the apex surface in a same relatively clean state. (4) For measurements with the probe-ball in close vicinity to the MWNT, a deviation from the F–N behavior for currents exceeding 1 $\mu$A was observed for approximately 20% of the MWNTs tested. The emission current increased more rapidly with voltage than expected from the F–N theory. This indicates some mechanical/physical changes to the MWNTs. We attributed this behavior to the straightening of some slightly bent MWNTs [e.g., nanotube 1 in Fig. 3(c)] under the electrostatic force from the probe to the nanotube.\textsuperscript{14} Taking the field for 1 $\mu$A, we have calculated this force to be $\approx 4 \times 10^{-7}$ N. (5) For $I_{\text{FE}} \geq 20$ $\mu$A, corresponding to an electrostatic force $\approx 8 \times 10^{-7}$ N, we have observed for some MWNTs a sudden shortening of the nanotube length (sharp drop in emission current) that we could attribute to either a fracture of the nanotube under the electrostatic force [probably at some crystallographic defect as seen at the middle of the nanotube 3 in Fig. 3(c)] or to a rapid field evaporation of the MWNTs during FE.

This preliminary study shows that each MWNT from a PECVD-deposited nanotube array acts as a conventional FE cathode up to 20 $\mu$A. The proposed cleaning procedure led to reproducible F–N characteristics with a $\phi = 4$ eV. The initial deviation from F–N type emission are due to artifacts from surface adsorption at the nanotube apexes. More importantly, we observed a variation $\Delta I/I$ of only 30% in the FE currents between the different MWNTs of the array after conditioning. This opens the possibility for using MWNTs as independent FE sources for massively parallel microguns.

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\begin{thebibliography}{9}
\bibitem{2} \textit{NANOLITH: Arrays of microguns for parallel e-beam nanolithography}, European IST project.
\bibitem{3} W. A. de Heer, A. Châtelin, and D. Ugarte, Science \textbf{270}, 1179 (1995).
\bibitem{4} IVMC, \textit{Technical Digest, 47th IVMC}, Aug. 2001, Davis, CA.
\bibitem{9} V. Semet and V. T. Binh (unpublished).
\end{thebibliography}