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Effects of Cs deposition on the field-emission properties of single-walled carbon-nanotube bundles

A. Wadhawan, R. E. Stallcup II, and J. M. Perez
Department of Physics, University of North Texas, Denton, Texas 76203

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We report the effects of Cs deposition on the field-emission (FE) properties of single-walled carbon-nanotube bundles. We observe that Cs deposition decreases the turn-on field for FE by a factor of 2.1–2.8 and increases the FE current by six orders of magnitude. After Cs deposition, the FE current versus voltage ($I-V$) curves show non-Fowler–Nordheim behavior at large currents, consistent with tunneling from adsorbate states. At lower currents, the ratio of the slope of the FE $I-V$ curves before and after Cs deposition is approximately 2.1. Exposure to N_2 does not decrease the FE current, while exposure to O_2 decreases the FE current. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1338493]

Carbon nanotubes have recently attracted considerable interest as electron field emitters due to their high-field-emission (FE) currents at low fields.[1,2] Potential technological applications include cold-cathode electron emitters in flat-panel displays, miniature microwave generators, monochromatic electron sources, and vacuum electronics.[3] According to the Fowler–Nordheim (FN) model,[4] FE from a metal or semiconductor is due to the tunneling of electrons from the material into vacuum under the influence of an electric field. The FE current depends strongly on the work function and geometry of the surface. The high-FE current from carbon nanotubes is thought to be due to the sharpness of tubes that enhances the local electric field.[1–3] However, the exact mechanism is not well understood. Cs deposition on field emitters such as Mo microtip arrays and diamond films has been reported to increase the FE current from these materials by lowering the work function.[5,6] It would, therefore, be interesting to study the effects of Cs on carbon nanotubes. Recent studies have shown that Cs deposition on single-walled carbon-nanotube (SWCN) bundles results in intercalation of Cs between the nanotubes,[7] and a decrease in the work function from 4.8 to 2.4 eV.[8] In this letter, we report the effects of Cs deposition on the FE properties of SWCN bundles.

The SWCN bundles were purchased from Tubes@Rice.[9] The material was grown using laser vaporization, purified to contain greater than 90 wt % SWCNs, and mixed in toluene to form a slurry.[10] The bundles had diameters of 5–20 nm and consisted of SWCNs having diameters of approximately 1.2 nm. The slurry was deposited on a conducting Si substrate and allowed to dry. The resulting film of bundles had a thickness of approximately 10 μm. To measure the FE properties of the film, an anode consisting of a 1.1-mm-diam platinum sphere was positioned 20–250 μm from the film. The platinum sphere was made by melting the end of a 0.02-in.-diam platinum wire and had an optically smooth surface.

Materials under the influence of an electric field emit electrons that tunnel through a potential barrier according to the FN equation[4]

$$I = A V^2 \exp\left(\frac{b\phi^{3/2}}{\beta V}\right),$$

where I is the current, A and b are constants, ϕ is the work function, V the applied voltage, and β the geometric enhancement factor. In general, the FE current is a sensitive function of the anode–film distance d. Therefore, it is important to precisely position the anode with respect to the film. We position the anode using a scanning tunneling microscopy (STM) system that uses a piezoelectric inchworm motor from Burleigh Instruments,[11] as shown in Fig. 1. The horizontal speed of the inchworm motor can be adjusted from approximately 2 to 0.5 mm/s. The position of the inchworm can be adjusted over 1 cm with an accuracy of ± 0.25 μm using a handset.[11] An anode and film are loaded on the inchworm and sample holder, respectively, and the system is operated in STM mode. The anode slowly approaches the film until tunneling occurs at $d \approx 0.5-1.0$ nm. The anode is then retracted a distance of 20–250 μm$\pm$0.25 μm from the film using the handset. Separate high-voltage electronics are used to measure the FE $I-V$ curves. Using this system, the anode can be accurately positioned for different films.

The inchworm system is housed in an ultra-high-vacuum (UHV) chamber equipped with a quadrupole mass spectrometer, Cs–metal dispenser from SAES,[12] and an Auger spectroscopy system (Omicron CMA-100) at a base pressure

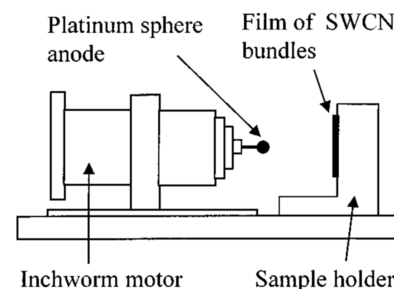

FIG. 1. Schematic of the positioning system consisting of a piezoelectric inchworm motor. The inchworm is operated as a scanning tunneling microscope to position the anode 0.5–1.0 nm from the film. The anode is then retracted 20–250 μm$\pm$0.25 μm from the film, and field-emission current vs voltage curves are measured.

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$<10^{-10}$ Torr. Auger spectroscopy is performed using an electron-beam current of 2 nA to prevent sample damage. The UHV chamber is connected to an UHV-compatible preparation chamber through an all-metal valve. In order to avoid contamination of the UHV system, the film is cleaned by heating it to 500 °C in the preparation chamber for 24 h. The film is then transferred to the UHV chamber using a linear translator without exposing the film to air. Using this procedure, the film is not observed to have any surface contaminants using Auger spectroscopy. FE $I-V$ curves of the clean sample are measured using the inchworm system as described above for $d=250$, 150, 75, and 20 μm. These FE $I-V$ curves are also consistent with a clean surface by not indicating FE from adsorbate states, as explained below. The sample is then transferred 2 cm from the Cs–metal dispenser, and Cs is deposited for 1 min. After Cs deposition, the film is transferred back to the inchworm system and FE $I-V$ curves are measured for the same values of d stated above. After the FE measurements, Auger spectroscopy is performed to determine the amount of Cs on the film. This procedure is repeated four times resulting in FE $I-V$ curves after total Cs deposition times of 1, 2, 3, and 4 min. The ratio of the Cs-to-carbon peak in the Auger spectra is 0.02, 0.06, 0.10, and 0.14 after 1, 2, 3, and 4 min of exposure, respectively. From these values, the surface concentration of Cs was estimated to be 3%, 6%, 11%, and 15%, respectively, using standard procedures outlined in the Handbook of Auger Electron Spectroscopy.[13] The resistance of the carbon-nanotube films was measured by allowing the anode to make contact with the film. The resistance before and after Cs deposition was measured to be 2 Ω, showing that Cs does not increase the conductivity of the samples.

Figures 2 and 3 show FE $I-V$ curves obtained as described above. In Figs. 2 and 3, the data are plotted $\ln(I/V^2)$ vs $1/V$ to allow comparison with the straight-line behavior predicted for FE by the FN equation. The insets in Figs. 2 and 3 show the $I-V$ curves plotted using a log–linear scale. The small current on the order of 5×10^{-13} A observed below the threshold voltage for FE is due to leakage across the connectors. The observed FE current has a weak dependence on d, consistent with geometric local-field enhancement. For example, for the sample exposed to Cs for 4 min, the threshold voltage for FE decreases from approximately 92 to 53 V as d changes by over an order of magnitude from 250 to 20 μm. As shown in Fig. 2(a) for $d=250$ μm, after 4 min of Cs deposition, the turn-on voltage for FE decreases by a factor of about 2.1 from 190 to 90 V, and the FE current increases by six orders of magnitude from 10^{-12} to 10^{-6} A at a voltage of 195 V. For the other anode–film distances, the turn-on voltage decreases by a factor of 2.4–2.8, and the FE current increases by six orders of magnitude. In Fig. 3(d), the "clean" and "1 min" curves almost overlap, unlike the curves for the larger distances. This is due to the fact that the data in Fig. 3(d) were taken at 20 μm and are susceptible to the film's local surface morphology as evidenced by the uneven shifts of the curves. At low currents, the $I-V$ curves show good agreement with the straight-line behavior predicted by the FN equation. At larger currents, the $I-V$ curves of the samples exposed to Cs show a departure from straight-line behavior towards smaller slope, as shown by the

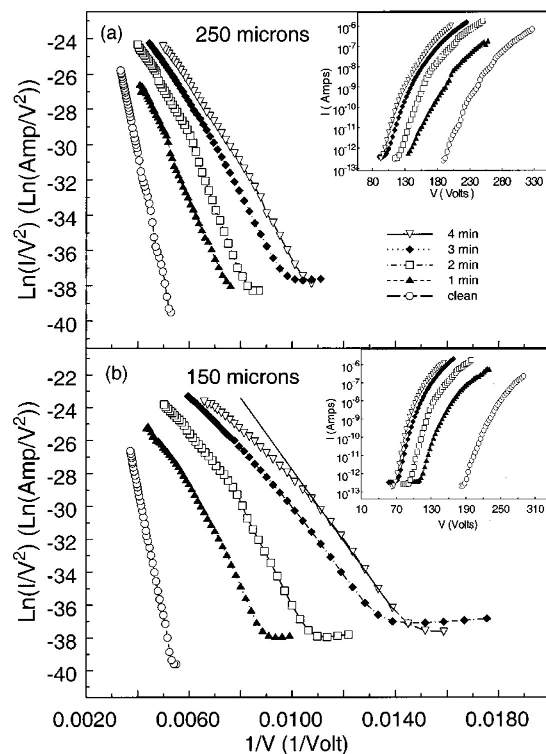

FIG. 2. Field-emission data from a film of SWCN bundles for a film that is clean and exposed to Cs for 1, 2, 3, and 4 min. The data are plotted to allow comparison with the Fowler–Nordheim model. The measurements are taken at anode–film distances of (a) $d=250$ μm and (b) $d=150$ μm. The straight-line fit in (b) shows the departure from Fowler–Nordheim behavior at large currents. The inset shows a plot of the field-emission current vs voltage using a log–linear scale.

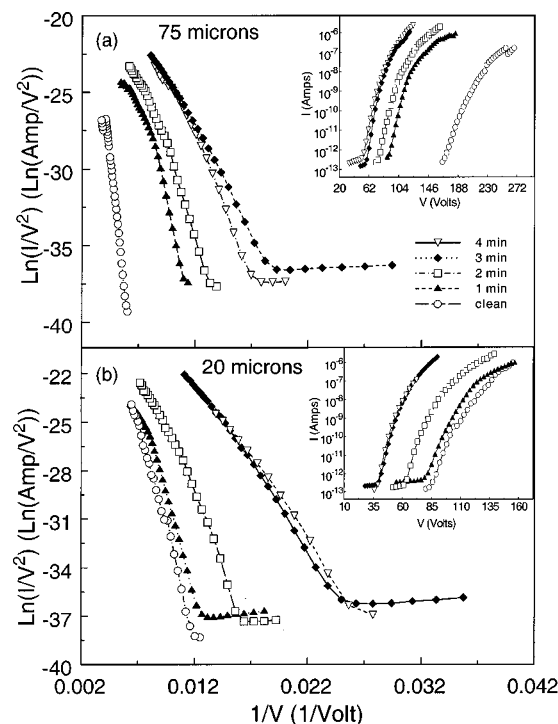

FIG. 3. Field-emission data from the film of SWCN bundles shown in Fig. 2 that is clean and exposed to Cs for 1, 2, 3, and 4 min. The data are plotted to allow comparison with the Fowler–Nordheim model. The measurements are taken at anode–film distances of (a) $d=75$ μm and (b) $d=20$ μm. The inset shows a plot of the field-emission current vs voltage using a log–linear scale.

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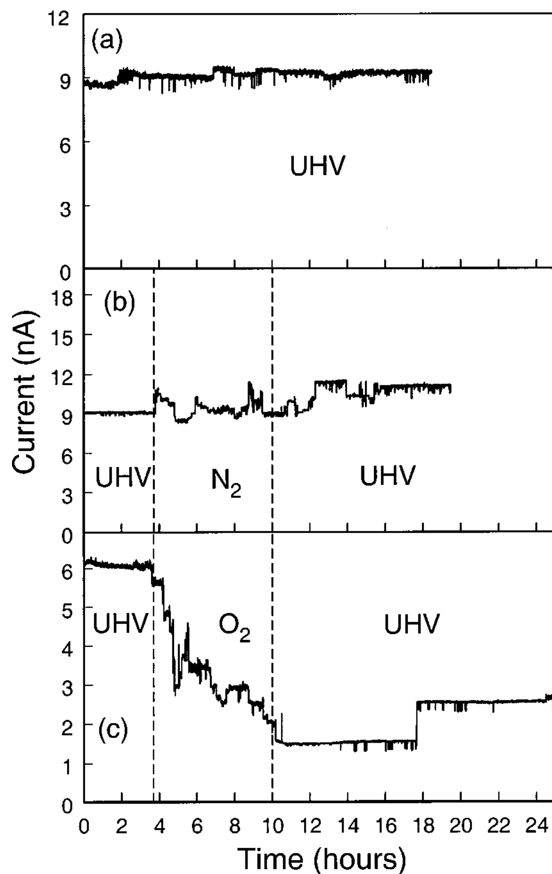

FIG. 4. Field-emission current as a function of time for a sample exposed to Cs for 4 min at $d=250$ μm. The current is measured (a) while the sample is in UHV, (b) during exposure to N_2 at 10^{-7} Torr, and (c) during exposure to O_2 at 10^{-7} Torr. In (b) and (c), the gas is introduced at the first dashed line and removed at the second dashed line.

straight-line fit in Fig. 2(b). This saturation effect is not observed for the clean nanotube sample, which agrees well with the FN equation even at high currents. A similar saturation effect has been observed in the FE $I-V$ curves of SWCNs at a pressure of 10^{-7} Torr,[14,15] and attributed to a current and field-induced decrease in tunneling from adsorbate states.[15] In Ref. 15, the adsorbates are due to H_2O in the vacuum container, and after high FE currents they observe a decrease in FE current and return to FN behavior due to desorption of the adsorbates. Since our experiments are performed in UHV and the saturation effect is not observed in the clean sample, we conjecture that the effect is due to the Cs adsorbates. At high currents (10^{-6} A), we do not observe a decrease in FE current and return to FN behavior in the $I-V$ curves shown in Figs. 2 and 3, showing that the Cs adsorbates are robust and not desorbed.

The FN equation shows that the value of $b\phi^{3/2}/\beta$ can be determined from the slope of the $\ln(I/V^2)$ vs $1/V$ curve. Assuming that β remains the same, the ratio of the work function before and after Cs deposition can be determined from the ratio of the slope before and after deposition.[5,16] We measure the slope of the straight-line behavior at low currents in the FE $I-V$ curves shown in Figs. 2 and 3. From these measurements, the ratio of the slope for the clean sample and the slope for the sample exposed to Cs for 4 min is found to be 1.8, 2.2, 2.5, and 2.0 for $d=250$, 150, 75, and 20 μm, respectively. It is interesting to note that the average of these values is 2.1 ± 0.3, in good agreement with the value of 2.0 for the ratio of the work function of SWCN bundles before and after Cs deposition measured using ultraviolet photoemission spectroscopy in Ref. 8.

We studied the effects of N_2 and O_2 gases on the FE properties of the SWCN bundles exposed to Cs for 4 min at $d=250$ μm. Figure 4 shows the FE current as a function of time in UHV, and during exposure to N_2 and O_2 at 10^{-7} Torr for about 6 h. Figure 4(a) shows that the FE current does not decrease in UHV. Figure 4(b) shows that upon introduction of N_2 there is an increase in fluctuation of the FE current. However, the FE current does not decrease in magnitude during the exposure. Figure 4(c) shows that exposure to O_2 decreases the FE current. The decrease is similar in magnitude to the decrease observed in the FE current from clean SWCNs during exposure to O_2.[17] Since the FE current does not fully recover after the O_2 is removed, the decrease is attributed to damage to the SWCNs.[17]

In summary, Cs deposition on SWCN bundles has a significant effect on the FE properties reducing the turn-on field by a factor of 2.1–2.8 and increasing the FE current by six orders of magnitude. The FE $I-V$ curves of samples exposed to Cs show a saturation effect at large currents attributed to the Cs adsorbates. At high currents, the Cs adsorbates do not desorb. At lower currents, the ratio of slopes before and after Cs deposition is approximately 2.1. The FE current does not decrease in UHV and during exposure to N_2, but decreases during exposure to O_2.

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