## Thermionic Emission of Single-Wall Carbon Nanotubes Measured

Researchers at the NASA Glenn Research Center, in collaboration with the Rochester Institute of Technology, have investigated the thermionic properties of high-purity, singlewall carbon nanotubes (SWNTs) for use as electron-emitting electrodes. Carbon nanotubes are a recently discovered material made from carbon atoms bonded into nanometer-scale hollow tubes. Such nanotubes have remarkable properties. An extremely high aspect ratio, as well as unique mechanical and electronic properties, make single-wall nanotubes ideal for use in a vast array of applications. Carbon nanotubes typically have diameters on the order of 1 to 2 nm. As a result, the ends have a small radius of curvature. It is these characteristics, therefore, that indicate they might be excellent potential candidates for both thermionic and field emission.

Three techniques for synthesizing such carbon nanotubes are arc discharge, chemical vapor deposition, and laser vaporization. The laser vaporization process was chosen in this study because of the large degree of control that can be exhibited on the final nanotube products. Variations in parameters such as target catalyst composition, laser beam power density, and synthesis temperature can influence the SWNT diameter distribution, production rate, and yield within the as-produced material.

Production of efficient thermionic devices depends on the use of low-work-function materials as electron emitters. For single-wall nanotubes, work function has been determined using a number of techniques. Ab initio calculations predict a work function of 3.75 eV for closed-ended single-wall nanotubes. In these studies, we used the thermionic emission of purified laser-vaporization-produced single-walled nanotubes to experimentally measure their work function.



SEM micrograph of purified nanotube paper.

All materials were synthesized using pulsed-laser synthesis with a 755-nm Alexandrite laser. Laser pulse duration was set at 100  $\mu$ sec with a repetition rate of 10 Hz, and the nanotubes produced were purified to remove metal catalyst impurities and extraneous carbonaceous material by reflux in nitric acid, followed by thermal oxidation in 20-percent O<sub>2</sub> ambient and annealing in argon at 1200 °C. The purification procedure results in a "paper" in which the nanotubes are the fibers. A representative scanning electron microscope (SEM) image of the resultant SWNTs is shown in the preceding figure.

So that the thermal emission could be measured, the nanotube paper was used as the electron emitter in a parallel plate configuration with a tantalum collector. The nanotube paper was held in good thermal contact to a ceramic boron nitride heater capable of providing measurement temper-atures up to 1300 °C. All measurements were taken in a vacuum chamber with a pressure of  $1 \times 10^{-8}$  torr or lower. The tantalum anode was brought to a distance of 0.5 mm from the single-walled nanotube paper. Potentials ranging from 0 to 1100 V were applied in ascending 10-V increments. Emission was studied for temperatures ranging from 25 to 1207 °C.

The emission plots obtained from a purified nanotube paper are shown in the following graph. Significant thermionic emission is observed starting at around 700 °C.



Thermionic emission from purified carbon-nanotube paper.

By fitting the Richardson-Laue-Dushman equation for thermionic emission current to the experimental data, one can obtain a value for the work function of single-wall carbon nanotubes. Using this equation,

$$J = AT^2 e^{(-e^{\bullet}/kT)}$$

where *J* is the saturation current density, *A* is a universal constant (120 A·cm<sup>-2</sup>·K<sup>-2</sup>), *T* is temperature in kelvin, *e*<sub>j</sub> is the effective work function, and *k* is Boltzman's constant, one can obtain the work function by plotting  $\ln(J/T^2)$  versus -1/k*T*. The effective work function is then equal to the slope of the resultant line. The Richardson-Laue-Dushman plot for the SWNT paper is shown in the final graph. This plot indicates that the single-wall carbon nanotubes have an effective work function of 3.46 eV.



Richardson-Laue-Dushman plot for the purified laser-vaporized single-wall nanotube paper.

There are a large number of possible applications for carbon-nanotube-based electron emitters, including use as lightweight, low-power emission sources for electron-beam displays, x-ray sources, vacuum tubes for high-power microwave communication systems, and energy-generation devices. By developing a technique to produce a thin sheet of highly purified nanotube emitter and measuring the electron emission as a function of temperature and applied field strength, we are making significant progress toward the development of higher efficiency and greater power devices for NASA and commercial applications.

## **Bibliography**

Elich, Jeffrey, et al.: Single Wall Carbon Nanotube Thermionic Emitters. Paper presented at the 3rd Conference on Thin Films and Nanotechnology for Energy Conversion, Brook Park, OH, 2003. To be published in a special issue of Materials Science and Engineering B, summer 2004.

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