Direct Power Generation by Electron Emission from Novel Carbon Nanostructures

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This research examines a novel concept for direct thermal-to-electrical power generation. The concept involves gate-modulated vacuum electron emission from arrays of carbon-based nanostructured emitters, such as graphitic carbon nanofibers and diamond nanotips. Such structures have been shown to produce highly efficient field emission (i.e., high electrical current at low applied fields) for electrical device applications; however, the commensurate transport and conversion of thermal energy has not been previously explored in detail. The emission mechanism produces a stream of high-energy electrons from heated cathode tips. The unique features of nanoscale electron emission enable efficiencies that promise to make this technology uniquely suitable for both nanoscale energy delivery as well as larger scale applications, including conversion of solar energy and traditional fuel sources.

This research relies on specific geometric features that become enhanced at nanometer scales. Arrays of solid, carbon-based emitters with characteristic radii of order 10 nm or less have been fabricated and shown to produce highly efficient emission. The key contributors to this behavior appear to be a high level of graphitic bonding and local geometric features of the tip emitters. This research program explores the foundational mechanisms of nanoscale electron emission in order to describe and achieve the conditions for optimal electrical and thermodynamic performance. The objectives of this work are summarized as follows:

- Develop novel fabrication techniques for large-area arrays of nanoscale, carbon-based emitters for power generation.
- Generate new understanding of the fundamental thermodynamics of field emission from nanoscale emitters.
- Determine the influence of geometric parameters, dopant types and levels, electrical contact materials, surface treatments, and nanocrystalline structure on thermodynamic performance.
- Incorporate the above information into a theoretical/computational tool for predicting the power generation characteristics of field emission devices and for determining performance limitations.
- Develop physical prototypes to demonstrate thermodynamic performance over broad temperature ranges.
- Initiate a graduate student education program on nanotechnology within an existing interdisciplinary program.
- Engage business management students and the local business community in activities related to the commercialization of nanotechnology.

Fisher's group at Purdue is developing experimental tools for characterizing emission at elevated temperatures. Energy distributions are measured with a hemispherical energy analyzer (SPECS-Phoibos 100 SCD) built into a vacuum chamber that achieves 10^{-9} torr. The system achieves an energy resolution of less than 10 meV, sufficient to resolve quantum confinement effects produced by emitter materials. The group has also developed a model for thermionic emission based on the Non-equilibrium Green's Function Method and applied it to measured thermionic emission energy distributions. The group also measures current-temperature behavior, such as that shown in Figure 1 for thermionic emission.

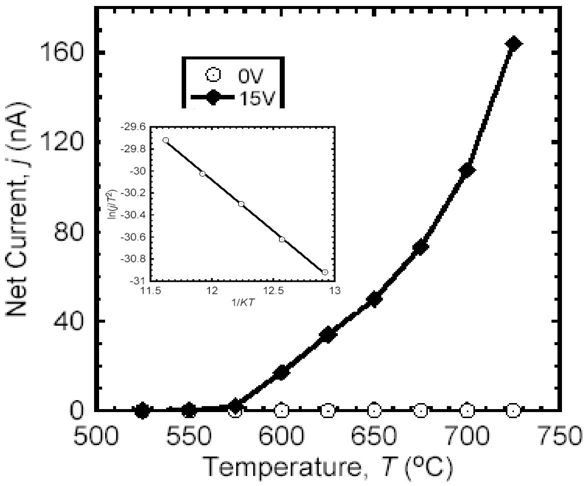

Figure 1. Thermionic current as a function of temperature for a boron-doped diamond film. Inset shows the related Richardson plot, indicating thermionc emission.

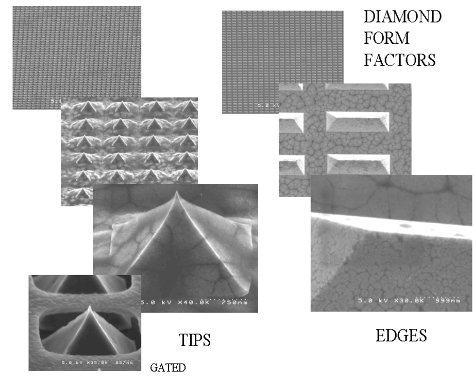

Figure 2. Various forms of molded diamond tip structures fabricated by plasma-enhanced chemical vapor deposition.

Davidson's group at Vanderbilt has continued to refine the morphologically engineered diamond nanostructures, "tips and edges" (see Figure 2) for optimum cold cathode configurations. Eliminating gate to cathode leakage remains a priority concern. A package for the emission devices is being developed so that effects can be examined outside vacuum chambers.

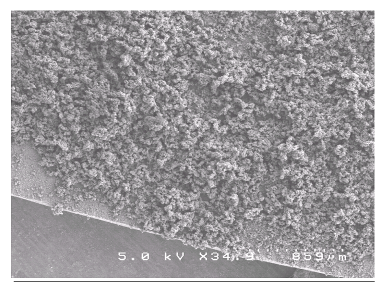

Figure 3. SEM image of a typical GCNF/Si wafer mat sample.

The Lukehart Group of this NIRT Team has prepared several graphitic carbon nanofiber samples to be examined for field emission. These samples are comprised of three types – pressed pellets of graphitic carbon nanofibers (GCNFs), GCNF mats grown on various Si wafer substrates, and pellets of GCNF/potassium metal intercalates. These specimens contain graphitic carbon nanofibers having either a herringbone or platelet atomic structure. Potassium intercalates include stage 1 (C_8K) and stage 2 ($C_{24}K$) compositions.

Material characterization is an important component of the research initiative. In order to understand and optimize the field emission process, it is essential to have a thorough knowledge of the physical, chemical, and electronic properties of the nanostructured carbon arrays (diamond or nanofibers). Swain's research group at Michigan State is applying traditional characterization techniques, such as scanning electron microscopy, Raman spectroscopy, x-ray photoelectron spectroscopy, x-ray diffraction, and secondary ion mass spectrometry, to evaluate the morphological, microstructural, and chemical properties of the different carbon architectures. They are also utilizing more non-traditional tools to study the physicochemical material properties, such as electrochemical methods of analysis and modification (see Figure 4), electrochemical atomic force microscopy, scanning electrochemical microscopy, and conductivity atomic force microscopy. Electrochemical reactions involve electron transfer between an electrode surface and a redox analyte (acceptor or donor) dissolved in solution. Electrochemical and scanning probe microscopy measurements provide information about the carbon nanoarchitecture surface chemistry, the nondiamond sp2 carbon content, the local density of electronic states, and the local electrical conductivity of the high aspect ratio features.

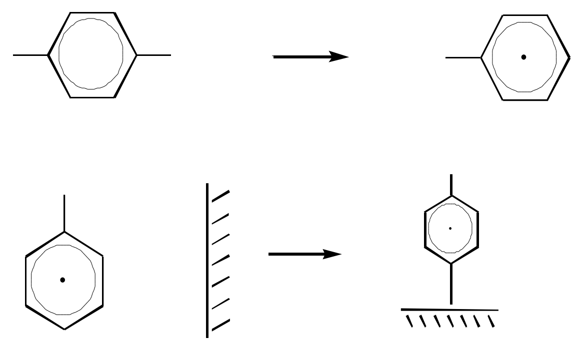

Figure 4. General scheme for the electrochemical-assisted modification of diamond surfaces via the reduction of phenyl-substituted diazonium salts, specifically, 1-nitro-4-azobenzene (NBD).

In support of the National Nanotechnology Initiative, we are implementing a program involving collaboration with the business community. In collaboration with Prof. Germain Böer of Vanderbilt's Owen School of Management and counterparts in Purdue's Krannert School of Management, we are recruiting and have recruited MBA students who have technical backgrounds, advanced degrees, and/or industrial experience in engineering or the sciences and who have an expressed interest in technology-based enterprises. These students are studying the business side of nanotechnology. A seminar series, organized by the PIs and business-school collaborators and co-sponsored by the Nashville Technology Council, on issues related to nanotechnology is in place. The first seminar was conducted at Vanderbilt and was well attended by interested MBA students.

For further information about this project, link to http://widget.ecn.purdue.edu/~tsfisher/nirt/.

Related Publications

J. A. Bennett, J. Wang, Y. Show, and G. M. Swain, "The Effect of sp^2-Bonded Nondiamond Carbon Impurity on the Physical and Electrochemical Properties of Boron-Doped Polycrystalline Diamond Thin-Film Electrodes", *J. Electrochem. Soc.*, submitted 2003.

T.S. Fisher, D.G. Walker, R.A. Weller, "Analysis and Simulation of Anode Heating from Electron Field Emission," *IEEE Transactions on Components and Packaging Technologies*, Vol. 26, No. 2, pp. 317-323, 2003.

S.H. Shin, T.S. Fisher, D.G. Walker, A.M. Strauss, W.P. Kang, J.L. Davidson, "High-Temperature Electron Emission from Diamond Films," *Journal of Vacuum Science and Technology-B*, Vol. 21, No. 1, pp. 587-592, 2003.

T.S. Fisher and D.G. Walker, "Thermal and Electrical Energy Transport and Conversion in Nanoscale Electron Field Emission Processes," *ASME Journal of Heat Transfer*, Vol. 124, No. 5, pp. 954-962, 2002.

T.S. Fisher, "Influence of Nanoscale Geometry on the Thermodynamics of Electron Field Emission," *Applied Physics Letters*. Vol. 79, No. 22, pp. 3699-3701, 2001.

J. A. Bennett, J. Wang, Y. Show, and G. M. Swain, "The Effect of sp^2-Bonded Nondiamond Carbon Impurity on the Physical and Electrochemical Properties of Boron-Doped Polycrystalline Diamond Thin-Film Electrodes", *J. Electrochem. Soc.*, submitted 2003.

D. Knigge and G. M. Swain, "Microcrystalline and Nanocrystalline Diamond Electrodes Chemically Modified with Nitrophenyl Groups", *Langmuir*, submitted 2003.