SESSION J18: Diamond for Thermionic Conversion and Electron Emission Chair: Jimmy Davidson Friday Morning, December 4, 2009 Back Bay A (Sheraton)

8:30 AM *J18.1

Thermionic Emission and Energy Conversion Based on Doped Diamond Films and Surfaces. Robert J. Nemanich¹, Griff L. Bilbro², Franz A. Koeck¹, Joshua R. Smith² and Yingjie Tang²; ¹Department of Physics, Arizona State University, Tempe, Arizona; ²North Carolina State University, Raleigh, North Carolina.

Thermionic electron emission from diamond surfaces is achieved with n-type doping, hydrogen termination, and control of the band bending and interface properties. Unlike field emission, the thermionic emission from the doped films and surfaces is essentially uniform over the surface. Photoemission results indicate work function values of less than 1.4 eV, which is one of the lowest of any material. Thermionic emission from nitrogen doped film structures are detected at temperatures as low as 200C. Results from single crystal and homoepitaxial N-doped surfaces confirm the fundamental emission processes. Theoretical analysis of an energy conversion device based on these films indicates that the negative electron affinity (NEA) provides a significant benefit to reducing space charge effects, and high efficiency cell designs have been developed. The substrate-film interface is established as a significant effect that limits the emission current density or Richardson constant. Energy conversion results are presented for N-doped films and specific applications are discussed. The major challenge to advancing this technology is the enhancement of the emission current density, and specific approaches are discussed. (Research supported through the ONR TEC MURI.)

9:00 AM J18.2

Phosphorus Doped Diamond Films for Thermionic Electron Emitter Application. Franz A. Koeck¹, Robert J. Nemanich¹ and Ken Haenen²; ¹Department of Physics, Arizona State University, Tempe, Arizona; ²Institute for Materials Research, Hasselt University, Diepenbeek, Belgium.

Thermionic electron emitters based on diamond rely on effects related to the emission barrier at the surface, band bending and doping in the film near the surface, and the interface to the substrate. The negative electron affinity (NEA) of H-terminated diamond surfaces can remove the surface barrier for emission as the vacuum level becomes located below the conduction band minimum (CBM). Recent advances have indicated that P-doped diamond has appropriate donor states for thermal promotion of carriers into the conduction band. In this study P-doped polycrystalline diamond films are evaluated for thermionic emission applications. The focus of this study is both on the surface properties and on the interface. Nanodiamond based pre-treatments were observed to result in a nanocrystalline diamond like morphology which adversely affects thermionic emission properties. Conversely, ultrasonication in a polycrystalline diamond based suspension is preferred as polycrystalline film morphology with clearly identifiable crystal facets occur after moderate growth times. Additionally, the substrate material strongly affects nucleation and growth properties. While a silicon substrate results in a delay of the nucleation process, metallic substrates prove advantageous in terms of P-doped diamond film growth. Exposure of the film surface to a hydrogen plasma induces an NEA characteristic and as a result electron emission can be observed at moderate temperatures. For oxygen terminated surfaces emission is well below the detection limit indicative of an increase in the surface emission barrier. The hydrogenated P-doped diamond surfaces exhibit short term emission stability up to 800 °C.

9:15 AM J18.3

Fabrication of Monolithic Field Emission Devices Consisting of Carbon Nanotubes Protruding from Diamond

Films for High Performance Cold Cathode Applications. Deepak Varshney², Vladimir Makarov², Puja Saxena², Brad R. Weiner^{1,3} and <u>Gerardo Morell</u>^{1,2}; ¹Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, Puerto Rico; ³Dept of Chemistry, University of Puerto Rico, San Juan, Puerto Ri

Solid state field emission devices are limited by the type and quality of their interfaces. Although, both, carbon nanotubes and doped diamond films have been identified as good field emission materials individually, their monolithic integration can simultaneously exploit their best features, and thus appears to be very promising. Doped diamond provides a robust material in good adhesion with the metallic substrate, while carbon nanotubes provide local field enhancement for low turn on fields. Monolithic CNT/diamond structures were fabricated and tested for their field emission properties and long term stability. Multilateral characterizations - including Raman, XPS, SEM, EELS, TEM, XPS - were employed to elucidate the compositional and structural properties of the monolithic high performance field emitting devices obtained. In this presentation we discuss the growth mechanism, the seamless integration of CNTs in diamond, the Fowler-Nordheim parameters and their interpretation, and the stability tests performed.

9:30 AM J18.4

Electron Current Amplification Using Single-Crystal CVD Diamond Films. <u>Joan E. Yater</u>, Jonathan L. Shaw, Kevin L. Jensen, James E. Butler, Tatyana Feygelson and Bradford B. Pate; Naval Research Laboratory, Washington, District of Columbia.

Diamond is a promising cold electron source due to the negative electron affinity (NEA) present at stable hydrogenated surfaces as well as the excellent electronic, thermal, and mechanical properties of the material. Although the absence of an internal electron supply has thus far impeded the development of NEA diamond emitters, there are still opportunities to exploit the exceptional secondary emission capabilities of NEA diamond. One such opportunity is the development of a high-gain current amplifier, which has the potential to increase the emission current from an external cathode by a factor of 50-100. By enhancing the performance of existing cathodes (e.g., field, photo, or thermionic emitters), the diamond amplifier would enable the development of various higherpower, higher-frequency vacuum electronic devices. In this study, we investigate the current amplification process in CVD diamond films using electron transmission spectroscopy. Specifically, we inject high-energy electrons into thin diamond films using a 0-20 keV electron gun, and we then detect and analyze the low-energy secondary electrons that are generated and transmitted through the films. In particular, the intensity and energy distribution of the transmitted electrons are measured as a function of the incident beam energy and current, and the electron transport behavior is analyzed using Monte Carlo simulations. In order to optimize the electron transport efficiency and transmission gain, the amplifiers are fabricated using high-purity, single-crystal diamond grown at NRL. Measurements will be presented from our initial amplifiers, which include both unbiased and biased structures, and the electron transport dynamics and emission characteristics will be evaluated as a function of bias voltage, film thickness, and impurity concentration.

9:45 AM J18.5

Thermionic Emission from Lithium Doped Nanodiamond. Tomas L. Martin^{1,2}, Gareth M. Fuge², Neil A. Fox^{1,2}, Roger Vincent¹, David Cherns¹ and Michael N. Ashfold²; ¹H.H. Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom; ²School of Chemistry, University of Bristol, Bristol, United Kingdom.

Diamond with n-type doping through Nitrogen or Phosphorus has shown promise as a low temperature thermionic emitter, giving workfunctions down to 1.29eV and 0.90eV respectively and significant emission at temperatures of 600°C and below^{1,2}. This paper examines an alternative approach in which Lithium is used as a potential n-type

dopant of diamond. With a theoretical level 0.1eV below the conduction band, interstitial Lithium has the potential to provide low workfunction materials but previous attempts have led to electrically inactive material. In this project, single crystal High Temperature High Pressure Type IIb nanodiamond powders have been successfully lithium doped using post-growth indiffusion of Lithium Hydride at temperatures of 700-900°C under a low pressure of inert gas. Subsequently the powders were washed to remove excess Lithium Hydride either using distilled water or by heating to 200°C in fuming nitric acid. Transmission Electron Microscopy studies showed remnants of Lithium Hydride after water washing but no trace of surface impurities after acid cleaning. The two powders were pressed into a electrode cylinder and heated with a field of 0-0.02V/micron applied to a metal collector anode 1mm away. Thermionic testing of the water washed powder under high vacuum showed significant emission currents at cathode temperatures greater than 560°C, reaching a current of 3.64mA/cm² at 793°C. Analysis using the fieldmodified Richardson equation showed a thermionic workfunction of 1.41 electronvolts. The acid cleaned powder showed an improved thermionic workfunction of 0.91eV, albeit with emission current an order of magnitude lower. This paper will illustrate the emission of these two materials with temperature and consider the reasons for their different characteristics. The potential of Lithium-doped diamond for use as a low temperature thermionic emitter will also be discussed. F.A.M. Koeck, R. Nemanich, Diamond Relat. Mater. 18 2-3 232-234 (2009) F.A.M. Koeck, R.Nemanich, A. Lazea, K. Haenen, Diamond Relat. Mater. 18 5-8 789-791 (2009)