Thermionic and Field Electron Emission Devices from Diamond and Carbon Nanostructures

Robert J. Nemanich, Griff L. Bilbro, , Eugene N. Bryan, Franz A. Koeck, Joshua R. Smith, Yingjie Tang Arizona State University, Tempe AZ; North Carolina State University, Raleigh, NC 27695-8202 E-mail: robert.nemanich@asu.edu

Abstract-Electron emission from carbon materials has been based on two effects: field enhancement from conducting nanostructures and barrier lowering due to the negative electron affinity of diamond surfaces. Moreover, n-type doping with P and N can enable a low work function. This presentation details the significant scientific issues related to thermionic and field electron emission and describes potential applications ranging from energy conversion, sensors, high power electronics, and nano electronics and photonics.

I. INTRODUCTION

Diamond and carbon nanostructures exhibit unique properties which have led to numerous studies of electron emission, and more recently thermionic emission. Research in field emission from carbon structures was first studied as a possibility for high resolution bright displays. More recently the materials have been considered for power electronics, space based thrusters and local x-ray sources. Thermionic emission applications include large area cathodes for microwave applications and direct heat to electrical energy conversion systems that could compete with thermo-electrics.

For field emission measurements, it is now widely accepted that field enhancement effects are the most significant in achieving the high emission currents.[1] Nanostructured and nanocrystalline films appear to be most appropriate for these applications. The negative electron affinity of diamond surfaces obtained with hydrogen termination is often cited as a primary effect for both field emission and thermionic emission. Other important effects include doping, contacts, and control of band bending. These effects are most relevant for thermionic emission. This presentation clarifies the effects that play the most significant roles in both field emission and thermionic emission from diamond and carbon nanostructures.

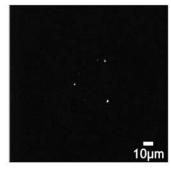
Both effects are important for different types of applications. Since the thermionic emission results are perhaps the most recent, we will concentrate on describing potential applications and devices based on thermionic electron emission from diamond based films.

II. EMISSION CHARACTERISTICS

A. Spatial Dependence:

One of the most direct ways to distinguish whether field enhancement or a reduced emission barrier are most critical for emission is evidenced in the emission spatial dependence.

*Contacting Author: robert.nemanich@asu.edu



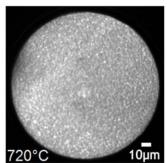


Fig. 1. High resolution electron emission microscopy image of the emission sites from a nanorystalline diamond film at an applied field of \sim 2 x 10^6 V/m (left) and the thermionic emission from a nitrogen doped diamond film at \sim 720C.

In most cases the emission sites are evident with projection imaging onto a phosphor screen. More advanced techniques such as field emission electron microsocopy or probing the emission with an AFM or STM shows a broad distribution of emission intensities from the different sites. Interestingly similar patterns have been reported for nanocrystalline diamond films, carbon nanotube mat type films and other carbon nanostructures. Emission site densities of >10⁵ cm⁻² are often evident with the high resolution techniques, while the low resolution projection approaches are dominated by the strongest emission characteristics. These types of patterns are characteristic of strong field enhancement.[1,2]

In contrast, imaging the thermionic emission from N-doped diamond shows essentially uniform emission over the whole as-grown surface.[3] This emission is enabled by the negative electron affinity of the surface. This aspect is clearly established by imaging the emission at temperatures above 700C where the image often suddenly disappears. This affect has been attributed to evolution of the hydrogen termination from the surface which increases the electron affinity from about -1.2 eV to ~0.5 eV for a clean surface.

B. Spectroscopic Measurements:

UV Photoemission spectroscopy, which measures the spectrum of the emitted electrons, was first employed to establish the work function and electron affinity of the surfaces. The energy spectrum of the emitted electrons can be employed to establish the work function and electron affinity of the surface. In general, this technique measures an average over the whole surface, and it has been argued that since

emission sites represent only a small fraction of the surface, they may not reflect the work function of the actual emission sites. This aspect can be obviated through the use of a grid near the surface to apply a field such that an emission peak is observed in addition to that excited with the photoemission. [4]

For B-doped diamond, this additional peak has a width of a few tenths of an eV and corresponds to electron states near the Fermi energy.[4] This peak establishes that the emission

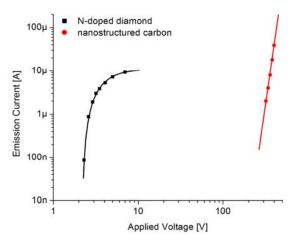


Fig. 2. Emission current versus applied voltage for field emission from nanostructured carbon film and thermionic emission from a N-doped diamond film..

originates from the valence band, and the photoemission indicates that the average work function of the surface is about 5 eV. However, the specific work function of the field emission sites cannot be determined with this approach.[1]

This issue is not so confusing for thermionic emission since the surface emits uniformly. Photoemission spectra obtained as a function of temperature, display the work function and the position of the Fermi level within the band gap. Moreover, at elevated temperature, the spectrum of the emitted electrons can be obtained without photo excitation, and here again the spectrum is a few tenths of an eV wide and appears to correspond to emission from the conduction band minimum. For nitrogen doped diamond films the thermionic emission is observed at 1.4 eV above the Fermi energy. [5]

C. Emission Current vs. Applied Voltage

Certainly the most common of all measurements for field emission are current vs. voltage which are then fit to the Fowler-Nordheim expression. For a system with unknown field enhancement it is not possible to directly deduce the work function of the emitting site. It is most common to assume that the work function of the surface is about 5eV, and then use the fitting to obtain the field enhancement factor. Attempts to measure the geometric field enhancement and then deduce the work function have been less successful.

For thermionic emission, there is typically an increase in the emission with applied voltage and then a nearly constant emission current independent of the applied voltage. The initial increase is typically ascribed to space charge effects.

D. Emission Current vs. Temperature

For field emission from surfaces with field enhancement, there is only a weak dependence of emission current on temperature. In contrast for doped diamond NEA surfaces, the emission current increases exponentially with temperature. Values as high as mA/cm² have been observed. Theoretical analysis suggest that even higher values are possible if the film resistance can be reduced to a low value.

E. Applications – Energy Conversion

An efficient thermionic emission surface could play a key role in the development of an efficient energy conversion device. Vacuum thermionic energy conversion devices consist of an electron emitter (heated) separated from an electron collector (cooled).[5] The potential that develops between the surfaces can be used for electrical power. Analysis suggests that emitter surfaces with a work funtions of ~1.4 eV could achieve a conversion efficiency greater than 20%.[6] Moreover, the NEA property of the diamond surface results in the emitted electrons having a significant velocity which mitigates space charge effects.

III. SUMMARY

This research has established the difference in the spatial emission characteristics of carbon films that would be appropriate for applications in field emission and thermionic emission devices.

ACKNOWLEDGMENT

This research was supported through the Office of Naval Research through the TEC MURI program.

REFERENCES

- L. Nilsson, O. Groening, P. Groening, O. Kuettel, and L. Schlapbach, "Characterization of thin film electron emitters by scanning anode field emission microscopy," *J. Appl. Phys.* 90, pp. 768-780, July 2001.
- [2] F.A.M. Kock, J.M. Garguilo, R.J. Nemanich, "Imaging electron emission from diamond film surfaces: N-doped diamond vs. nanostructured diamond," *Diamond Relat. Mater.* 10, pp. 1714-1718, Sep-Oct 2001.
- [3] F.A.M. Kock, J.M. Garguilo, B. Brown, R.J. Nemanich, "Enhanced low-temperature thermionic field emission from surface-treated N-doped diamond films," *Diamond Relat. Mater.* 11, pp. 774-779, Mar-Jun 2002.
- [4] C. Bandis, B.B. Pate, "Simultaneous field emission and photoemission from diamond," *Appl. Phys. Lett.* 69, pp. 366-368 Jul 1996.
- [5] F.A.M. Koeck, "Emission characterization from nitrogen-doped diamond with respect to energy conversion," R.J. Nemanich, *Diamond Relat. Mater.* 15, pp. 217-220 Feb-Mar 2006.
- [6] J.R. Smith, G.L. Bilbro, R.J. Nemanich, "Considerations for a high-performance thermionic energy conversion device based on a negative electron affinity emitter," *Phys. Rev. B* 76, Art Num: 245327, Dec 2007.