

Emission characterization from nitrogen-doped diamond with respect to energy conversion

Franz A.M. Koeck*, Robert J. Nemanich

North Carolina State University, Department of Physics, Raleigh, NC 27695-8202, USA

Available online 26 September 2005

Abstract

Vacuum thermionic energy converters utilize electron emissive materials as a key component in the transformation of thermal into electrical energy. Electron emission from nitrogen-doped diamond films was characterized with respect to the thermionic emission relation derived by Richardson–Dushman. Key parameters, which describe the emitter material, are the work function ϕ and the Richardson constant A . A fitting procedure has been employed to determine ϕ and A for nitrogen-doped diamond. However, a simultaneous solution to the Richardson–Dushman relation was limited due to the strongly coupled parameters ϕ and A . Additionally, the emission was characterized at various applied fields indicating a change in the electronic structure of the material contrary to classical thermionic emitters.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Efficient energy sources are of ongoing interest due to increasing power demand of mobile electronic devices. Conceptually, thermionic energy conversion can provide means for the design of compact and mobile power sources. Here, an electrode at elevated temperatures, the emitter, is separated from a cooler counter-electrode, the collector, by a vacuum gap. A self-generated thermionic voltage, typically of the order of <1 V appears then across the gap with a distance of <500 μm [1–3]. The vacuum interspace provides a thermal barrier between the hot and cold sides and an electrical current can be established by connecting both electrodes.

Thermionic emission and its corresponding functionality was first described by Richardson and Dushman and is condensed in the expression

$$J(T) = AT^2 e^{-\frac{\phi}{k_B T}}, \quad (1)$$

where the emission current density J [A/cm^2] is described in terms of the work function ϕ [eV], the Richardson constant A [$\text{A}/\text{cm}^2 \text{K}^2$], the temperature T [K] and the Boltzmann constant k_B [4]. An evaluation of Eq. (1) presents the work function ϕ

as the barrier for emission and Richardson's constant A as a measure of the emission current density for a given material. This parameter, A , is ideally determined from a collection of fundamental constants and quantified as

$$A = \frac{emk_B^2}{2\pi^2\hbar^3}, \quad (2)$$

where m is the electron mass and \hbar is the Planck constant. A is furthermore determined by surface structural properties of the emitter, which can apparently lead to a variation from its theoretical value of $123 \text{ A}/\text{cm}^2 \text{K}^2$. For tungsten with a work function of 4.52 eV, the constant A has been experimentally determined to be $\sim 60 \text{ A}/\text{cm}^2 \text{K}^2$. However, efficient thermionic emitters require a reduced work function material and this has been accomplished by modifying a tungsten matrix through impregnation with barium (W+Ba) or thorium (W+Th). The work function is then lowered to 2.7 eV for W+Th and 1.6 eV for W+Ba [5]. This reduction in the work function is accompanied by a change of the Richardson constant, namely a decrease to 4 and $1.5 \text{ A}/\text{cm}^2 \text{K}^2$ for W+Th and W+Ba, respectively. Another low work function emitter ($\phi = 1.5 \text{ eV}$), BaO, has been characterized by a Richardson constant of $0.1 \text{ A}/\text{cm}^2 \text{K}^2$ [6]. It is evident that the empirical value for A can differ several orders of magnitude from its theoretical counterpart.

* Corresponding author.

E-mail address: fakoeck@ncsu.edu (F.A.M. Koeck).

Novel material systems exhibiting low work functions as well as intrinsic space charge impeding properties could motivate a new generation of compact and mobile thermionic energy converters. One promising candidate is nitrogen-doped diamond, which has been shown to exhibit thermionic emission at temperatures considerably less than 1000 °C [7]. In this study we report on thermionic emission measurements and then fit the data to the Richardson expression to explore the relation of ϕ and A to the observed emission.

2. Experimental setup

Nitrogen-doped diamond films were synthesized utilizing plasma-assisted chemical vapor deposition. The films were deposited on 1-in. diameter polished molybdenum disks due to their lower electrical resistance. Pretreatment included a 30-min ultrasonic abrasion step in a diamond/zirconium/methanol suspension with 0.1 μm diamond and 30 μm zirconium powder. [8] The sample was then rinsed in methanol, dried with nitrogen gas and loaded into the CVD reactor.

The emitter structure was comprised of an initial nucleation layer synthesized with 400 sccm hydrogen and 8 sccm methane at 20 Torr chamber pressure, 600 W microwave power and ~ 700 °C substrate temperature. Laser reflectance interferometry was employed to monitor nucleation and once the initial layer was established process parameters were adjusted for the nitrogen-doped diamond layer: 437 sccm hydrogen, 2.5 sccm methane, 60–100 sccm nitrogen, 50 Torr chamber pressure, 1300 W microwave power and ~ 900 °C substrate temperature. Sample preparation was concluded by a 1-min hydrogen passivation step where methane and nitrogen flow was terminated, chamber pressure was dropped to 20 Torr and microwave power reduced to 600 W. The final film thickness was determined by in situ laser interferometry to be ~ 0.3 μm .

Electron emission measurements from films grown on molybdenum were performed in a thermionic emission system providing a UHV environment for sample characterization. The system is comprised of a radiatively heated sample stage, a cooled, movable (in all 3 spatial directions) collector and a Stanford Research[®] current/voltage source unit. The base pressure in the chamber was $< 5 \times 10^{-10}$ Torr.

3. Results and discussion

One of the main emission-governing properties of diamond is the ability for its surfaces to gain a negative electron affinity (NEA) where the vacuum level is located below the conduction band minimum (CBM) of the surface. This provides means of efficient carrier discharge from the solid due to the absence of a surface barrier for emission. For diamond and diamond films a NEA surface can be induced by exposure to hydrogen plasma [9]. The nitrogen-doped films exhibit a ‘cauliflower-like’ morphology and the Raman spectra exhibit a peak at 1332 cm^{-1} due to diamond along with features due to sp^2 bonding. The film characterization has been reported in more detail elsewhere [10]. Typical nitrogen doping concentrations of up to $4 \times 10^{19} \text{ cm}^{-3}$ have been reported elsewhere [11]. It is still

difficult to determine if the N atoms reside in the diamond grains or in the boundaries.

Thermionic emission from hydrogen-passivated diamond surfaces is characterized by spatial uniformity in contrast to localized emission for other carbon-based materials, e.g. nanocrystalline diamond and CNT films [12]. The emission behavior can be visualized by electron emission microscopy which allows real-time observation of surface processes and has been shown in more detail elsewhere [13]. The emission current for a nitrogen-doped diamond film on molybdenum as a function of temperature is recorded and the corresponding data plot is shown in Fig. 1. Thermionic electron emission commences at temperatures as low as ~ 520 K and increases with temperature.

Characterizing the observed thermionic emission from nitrogen-doped diamond films is understood in terms of material constants, A and ϕ , by fitting the data to the Richardson formula. The fitting procedure substantiates the linked nature of A and ϕ where a reduction in the work function is accompanied by a diminished Richardson constant. While a Richardson constant of $10 \text{ A/cm}^2 \text{ K}^2$ is coupled with a work function of ~ 1.8 eV, the datafit with a work function of ~ 1.5 eV is then linked to $A=0.1 \text{ A/cm}^2 \text{ K}^2$. Thus, for a nitrogen-doped diamond film on molybdenum, a work function in the range of 1.5–1.9 eV can be extracted from the dataset. This is in accordance with the doping level of single substitutional nitrogen in diamond which has been reported at 1.7 eV below the conduction band minimum [14]. Elsewhere the ‘effective’ work function is defined as the work function determined via the theoretical Richardson constant of $A=123 \text{ A/cm}^2 \text{ K}^2$ [15]. This approach results in an ‘effective’ work function for the nitrogen-doped diamond film of 2.0 eV.

For a flat surface thermionic emitter described by Ref. [1] the emission current is independent of the extraction voltage for weak applied fields E , i.e. if

$$\pi \cdot h_0 \ll 1, \quad (3)$$

where h_0 is defined by Modinos as

$$h_0 \equiv \left(\frac{E \hbar^4}{m^2 e^5} \right)^{1/4} \frac{(e^3 E)^{1/2}}{\pi k_B T}. \quad (4)$$

At a bias of 10 V applied across a 1-mm emitter–collector gap, the electric field corresponds to 0.01 V/ μm and with $T \approx 1000$ K Eq. (4) is satisfied and holds true for applied fields well above 100 V/ μm . The thermionic emission from a nitrogen-doped film has been measured at $T=958$ K as a function of applied field and the result is shown in Fig. 2.

As shown in Fig. 2, the emission current increases significantly with bias and saturates at a field of ~ 0.2 V/ μm . At the saturation level the emission current density corresponds to $\sim 0.005 \text{ A/cm}^2$ at an emitter temperature of 958 K. While the theoretical description for thermionic emitters is formulated for a metallic emitter, emission from a semiconductor involves phenomena related to the intrinsic electronic structure of the conduction band. Moreover, two properties are of crucial

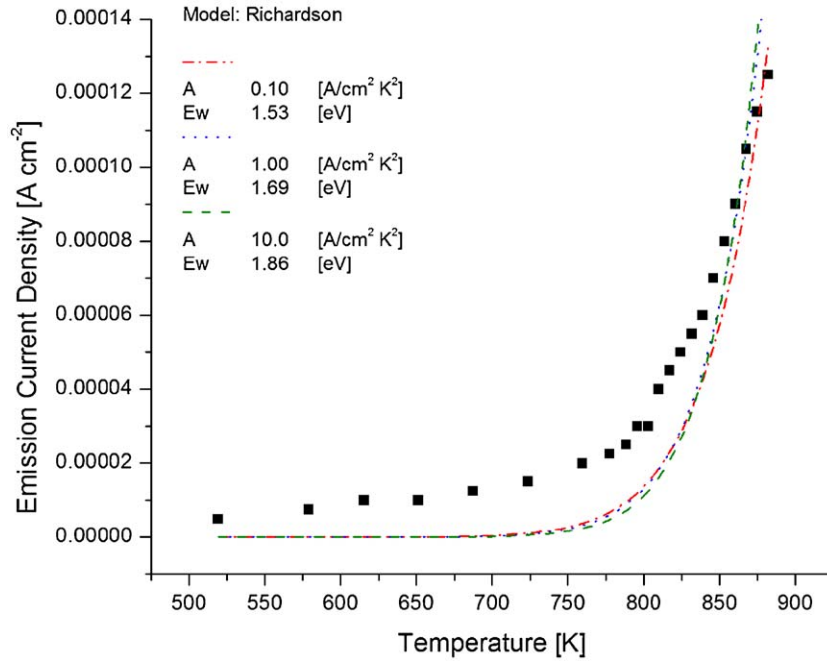


Fig. 1. Thermionic electron emission from a nitrogen-doped diamond film [squares] and fits to the Richardson equation using three values of the Richardson constant, A.

importance to the emission characteristics, the negative electron affinity (NEA) surface and the band bending at the surface. The amount of upward band bending for hydrogenated, nitrogen-doped (100) diamond has been estimated to be in the order of ~ 1.7 eV for a donor concentration of $\sim 10^{20}/\text{cm}^3$ [16]. As the band bending at the surface increases the effective work function will increase accordingly thus raising the emission barrier. Exposing this surface to an electric field will shift the upward band configuration due to

penetration of the field into the solid and as a result a reduced emission barrier may be observed. Exploitation of this phenomenon in a thermionic converter configuration is possible through fractional utilization of the internal field by adjusting emitter–collector spacing and resistivity of the circuit, i.e. predominantly the load.

The potential of nitrogen-doped diamond films as thermionic emitter materials is evident from the observed emission and the low possible work function. Further studies are

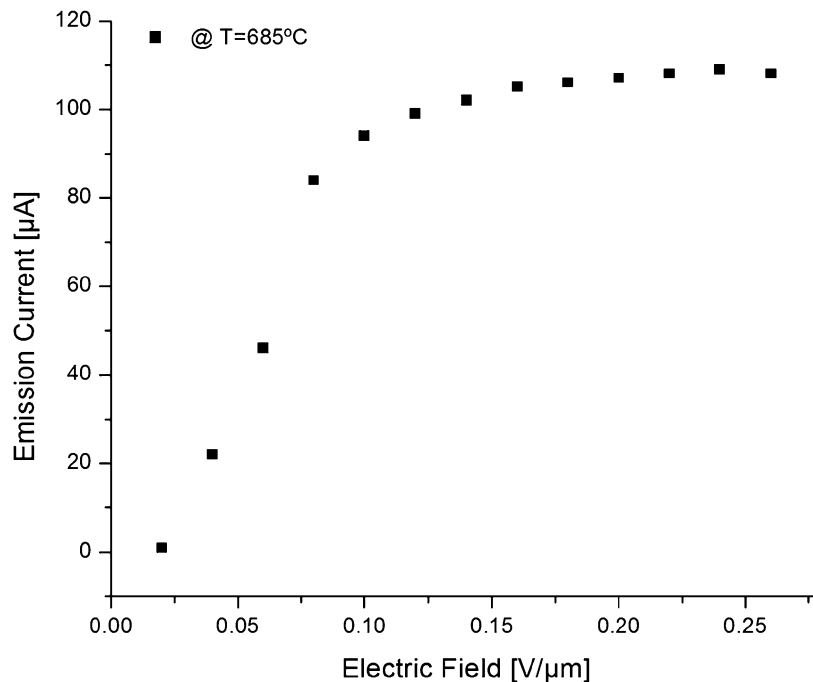


Fig. 2. Dependence of the thermionic emission current on the applied field at elevated temperatures for a nitrogen-doped diamond film on a Mo substrate.

necessary to determine the interplay between Richardson's constant and the work function.

4. Conclusion

Nitrogen-doped diamond films with a negative electron affinity (NEA) surface characteristic were synthesized on molybdenum and silicon substrates by plasma-assisted chemical vapor deposition. These films displayed thermionic electron emission at temperatures less than 900 K. The results were fit to the Richardson expression and the values of ϕ and A were found to be linked. The fits indicated values in the range from 1.5–1.9 eV and 0.1–10 A/cm² K², for ϕ and A , respectively. This low work function emission from nitrogen-doped diamond films could be suitable for application in a thermionic converter.

Acknowledgement

This research was funded by the ONR under the TEC-MURI project.

References

- [1] J. Alvarez-Ramirez, H. Puebla, G. Espinosa, *Annals of Nuclear Energy* 28 (2) (2001 Jan) 93.
- [2] V.A. Koryukin, *Atomic Energy* 90 (1) (2001 Jan) 1.
- [3] M.S. El-Genk, Y. Momozaki, *Energy Conversion and Management* 43 (7) (2002 May) 911.
- [4] A. Modinos, *Field, Thermionic, and Secondary Electron Emission Spectroscopy*, Plenum Press, New York, 1984.
- [5] R. Decher, *Direct Energy Conversion*, Oxford University Press, New York, 1997.
- [6] A.W. Culp, *Principles of Energy Conversion*, McGraw-Hill, 1979.
- [7] F.A.M. Koeck, J.M. Garguilo, R.J. Nemanich, *Diamond and Related Materials* 13 (11–12) (2004 Nov–Dec) 2052.
- [8] A.K. Dua, M. Roy, J. Nuwad, V.C. George, S.N. Sawant, *Applications of Surface Science* 229 (2004) 254.
- [9] P.K. Baumann, R.J. Nemanich, *Journal of Applied Physics* 83 (4) (1998 Feb) 2072.
- [10] M. Park, A.T. Sowers, C. Lizzul Rinne, R. Schlessler, L. Bergman, R.J. Nemanich, Z. Sitar, J.J. Hren, J.J. Cuomo, *Journal of Vacuum Science & Technology B* 17 (2) (1999 Mar–Apr) 734.
- [11] J. Mort, M.A. Machonkin, K. Okumura, *Applied Physics Letters* 59 (1991) 3148.
- [12] F.A.M. Köck, J.M. Garguilo, R.J. Nemanich, *Diamond and Related Materials* 14 (3–7) (2005 Mar–Jul) 704.
- [13] F.A.M. Köck, J.M. Garguilo, B. Brown, R.J. Nemanich, *Diamond and Related Materials* 11 (2002 Mar–Jun) 774.
- [14] R.G. Farrer, *Solid State Communications* 7 (1969) 685.
- [15] G. Gaertner, P. Geittner, D. Raasch, *Applied Surface Science* 201 (2002) 61.
- [16] L. Diederich, O.M. Küttel, P. Aebi, L. Schlapbach, *Surface Science* 418 (1998) 219.