Thermionic Converters Based on Nanostructured Carbon Materials

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Abstract. Thermionic energy converters are based on electron emission through thermal excitation and collection where the thermal energy is directly converted into electrical power. Conventional thermionic energy converters based on emission from planar metal emitters have been limited due to space charge. This paper presents a novel approach to thermionic energy conversion by focusing on nanostructured carbon materials, sulfur doped nanocrystalline diamond and carbon nanotube films as emitters. These materials exhibit intrinsic field enhancement which can be exploited in lowering the emission barrier, i.e. the effective work function. Moreover, emission from these materials is described in terms of emission sites as a result of a non-uniform spatial distribution of the field enhancement factor. This phenomenon can prove advantageous in a converter configuration to mitigate space charge effects by reducing the transit time of electrons in the gap due to an accelerated charge carrier transport.

Keywords: Diamond, doping, CVD, electron emission, energy conversion.
PACS: 79.40.+z, 79.70.+q.

INTRODUCTION

Initial thermionic energy converters (TEC) utilized planar metal based emitters which resulted in high operating temperatures as well as performance limitations due to space charge effects. However, lifetime and reliability of these converters encouraged deployment to space missions with its most prominent representative developed under the TOPAZ program (Alvarez-Ramirez, Puebla and Espinosa, 2001).

The high operation temperature of these systems significantly limited their application. However, the fundamental TEC configuration can allow the construction of a compact and mobile energy transformer that could operate at temperatures <1000 ºC. Basically, it is comprised of an electrode at elevated temperatures, the emitter, which is separated from a cooler counter-electrode, the collector, by a vacuum gap. Establishment of a temperature difference between emitter and collector results in a self generated thermionic voltage typically of the order of <1 V across the gap of <500 μm (El-Genk and Momozaki, 2002). The vacuum interspace provides a thermal barrier between hot and cold side and an electrical current can be established by connecting both electrodes.

In order to increase the efficiency and reduce the operating temperature of a conventional converter, an evaluation of key parameters demonstrated the need for low work function emitters and the means of reducing the space charge effect. This phenomenon is most significant for planar emitter geometries where a small surface roughness does not significantly alter the thermionic emission behavior. Introducing surface features with a high aspect ratio, i.e. tips, results in a geometrically non-planar emitter geometry. Thermionic emission from such a structure differs significantly from its planar counterpart and is strongly dependent on the extraction field. However, the high aspect ratio of a feature alone does not constitute a change in thermionic emission (Kan et al., 2003). Nanocrystalline diamond films typically exhibit an RMS roughness of 10 – 200 nm depending on the methane concentration during deposition (Yoshikawa, Morel and Koga, 2001; Soo-Hyung, Tae-Hoon and Jin-Seok, 2003). The film surfaces can thus be considered planar for emission purposes. Utilizing field enhancement based emitters would result in a configuration schematized in Figure 1. The emitter (hot side) is opposed by a cooler collector through a vacuum gap and their respective work functions are Φ_E and Φ_C. As the emitter is characterized by field enhancing structures, the potential will assume a distribution as shown in Figure 1. At the emitter-vacuum boundary, the internal field is

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significantly enhanced resulting in an accelerated transport of electrons. This effect reduces the transit time of charge carriers in the gap and thus mitigates space charge effects. Moreover, the strongly enhanced field at the surface results in a diminished emission barrier. The desired field distribution across the vacuum gap can be achieved by utilizing a fraction of the self-generated field through matching of the load resistance with the thermionic converter. Previously, introducing ionized vapor (Cs) into the gap was found to reduce this space charge phenomenon but at the cost of system complexity by utilizing this gaseous species. Additionally, the vapor pressure dominated the overall system performance and an operating temperature above 1100 ºC was required (Paramonov and El-Genk, 1997).

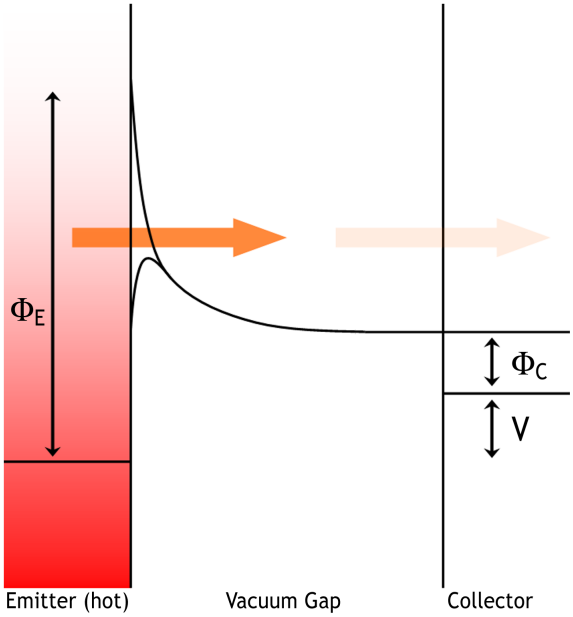

FIGURE 1. Schematic Band Diagram of a Thermionic Converter Utilizing a Field Enhancement Based Emitter to Mitigate Space Charge and Reduce the Work Function of the Emitter.

It is evident that the elimination of ionized vapors in the converter operation mode could result in the design of compact devices. Simultaneously, employing novel materials which exhibit low effective work functions as well as intrinsic space charge impeding properties could enable efficient, mobile energy sources. Combining a field enhancement based emitter with a low work function collector in a vacuum environment present the basic thermionic cell. The vacuum gap size can then be adjusted to meet electron emission characteristics of the emitter. This paper reports on thermionic emission characteristics of nanostructured carbon materials, i.e. sulfur doped nanocrystalline diamond and carbon nanotube (CNT) films with respect to energy conversion applications at temperatures considerably less than 1000 ºC.

Background

Electron emission in general can be described in terms of the extraction mechanism, i.e. by tunneling processes due to an applied electric field or thermionic phenomena due to thermal excitation of electrons. Exposing the emitter surface to an electric field will induce an electric current which obeys the law of Fowler-Nordheim (1928) and is given by:

$$J(F) = A' F^2 e^{\frac{-B'\varphi^{3/2}}{F}}, \tag{1}$$

$$A' \equiv e^3 \Big/ \left[16\pi^2 \hbar \varphi t^2 \left(\frac{\sqrt{e^3 F}}{\varphi} \right) \right], \tag{2}$$

and

$$B' \equiv \frac{4}{3e} \left(\frac{2m}{\hbar^2} \right)^{1/2} v \left(\frac{\sqrt{e^3 F}}{\varphi} \right), \tag{3}$$

with v(y) and t(y) tabulated functions which can be found elsewhere (Modinos, 1984). The Fowler-Nordheim relation (1) was derived for a zero-temperature electron distribution and thus does not consider a thermionic component to the emission. However, plotting $\ln(J/F^2)$ versus 1/F allows determination of the work function φ if the local field F at the emitter is known. While the applied field F for planar geometries is uniform over their surface, nanostructured materials exhibit a strong variation in the local field distribution. Field enhancing structures, described by the field enhancement factor β, modify the applied field F to $\beta(x,y)\cdot F$, where the field enhancement factor has become a spatially dependent function. Assessing the work function from a current / voltage data set for a given material involves a fitting procedure using Eq. (1) which requires knowledge about the field enhancement factor β. Thus, a simultaneous computation of φ and β is possible but with limitations.

Field independent electron emission by thermal excitation has been described by Richardson (1925) and Dushman (1923) in the relation:

$$J(T) = AT^2 e^{-\frac{\varphi}{k_B T}}, \tag{4}$$

The emission current is then determined by two parameters, the work function φ as the barrier for emission and Richardson's constant A as a parameter of the emission current density for a given material. A theoretical derivation of A has shown its value to be fundamentally described by:

$$A = \frac{emk_B^2}{2\pi^2 \hbar^3}, \tag{5}$$

where m is the electron mass, and $\hbar$ the Planck constant. Moreover, a surface morphological contribution to the value of A results in a variation from its theoretical value of 123 $A/cm^2 K^2$. To account for field effects in thermionic emission, the Richardson-Dushman equation was modified by adding a field dependent term, $(e^3 \cdot F)^{1/2}$, in the exponent which effectively results in a reduction in the work function, i.e. the effective work function of the emitter. This relation is also referred to as the Schottky formula:

$$J(F,T) = AT^2 e^{-\frac{\varphi - \sqrt{e^3 F}}{k_B T}}. \tag{6}$$

Electron emission from sulfur-doped nanocrystalline diamond as well as carbon nanotube films was characterized in terms of the field modified Richardson relation. In this study we attempted to determine the field enhancement factor and the work function for sulfur doped nanocrystalline diamond films. We have also determined the barrier reduction for emission due to field enhancement effects.

EXPERIMENTAL

Sulfur doped nanocrystalline diamond films were synthesized utilizing plasma assisted chemical vapor deposition. The films were deposited on 25.4 mm diameter Mo substrates. Pretreatment included a 30 minute ultrasonic abrasion step in a diamond/titanium/methanol suspension with 0.1 μm diamond and 30 μm titanium powder. (Shima, Chakk and Hoffman, 2000) The substrate was then rinsed with methanol, dried with nitrogen gas and loaded into the CVD reactor.

The sulfur source was a 50ppm hydrogensulfide in hydrogen (H_2S/H_2) mixture. The emitter films were synthesized with 5 to 40 sccm of the (H_2S/H_2) mixture and 20 sccm methane at 2665 Pa chamber pressure, 900 W of microwave power, and ~900 ºC substrate temperature. Laser reflectance interferometry was employed to monitor film growth in situ. Sample preparation was concluded by simultaneously terminating gas flows, shutting off the microwave plasma and substrate heating. The final film thickness was determined by in situ laser interferometry to ~0.3 µm.

Carbon nanotube (CNT) films were prepared in the same plasma assisted CVD reactor with sputtered iron as the catalyst and 1 inch diameter molybdenum as substrate material. Precursor gases were ammonia and acytelene and the growth time was 30 minutes (Wang et al., 2004).

Electron emission measurements from films grown on molybdenum were performed in a thermionic emission system providing a ultra-high vacuum 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 < $6x10^{-8}$ Pa.

RESULTS AND DISCUSSION

Nanostructured carbon materials, i.e. nanocrystalline, ultrananocrystalline and carbon nanotube (CNT) films exhibit electron emission as a result of a non-uniform distribution of the field enhancement factor β. This singularity can be directly observed in a projection of the emissivity where individual emission sites appear as bright sources. In a different study, the size of a single emission site has been estimated to be ~ 10 nm while no direct correlation between surface topography and emissivity could be observed (Köck, Garguilo and Nemanich, 2004). This indicates that field enhancing characteristics are not solely governed by structural properties where high aspect ratio features such as tips exhibit high field enhancement factors.

For a sulfur doped nanocrystalline diamond film on molybdenum current/voltage sweeps were recorded at various temperatures, and the result is shown in Figure 2. The emission current increases with emitter temperature and with a shift to higher temperatures the emission current increases at a higher rate. Concurrently, the data indicates a diminished threshold field to values considerably less than 1 V/µm. This observed emission behavior could prove advantageous in a thermionic energy converter configuration where a small, self generated electric field appears across the vacuum gap. A fraction of this field could then be utilized to exploit the emission behavior of the nanostructured emitter where a lowered threshold field would result in an increased emission current.

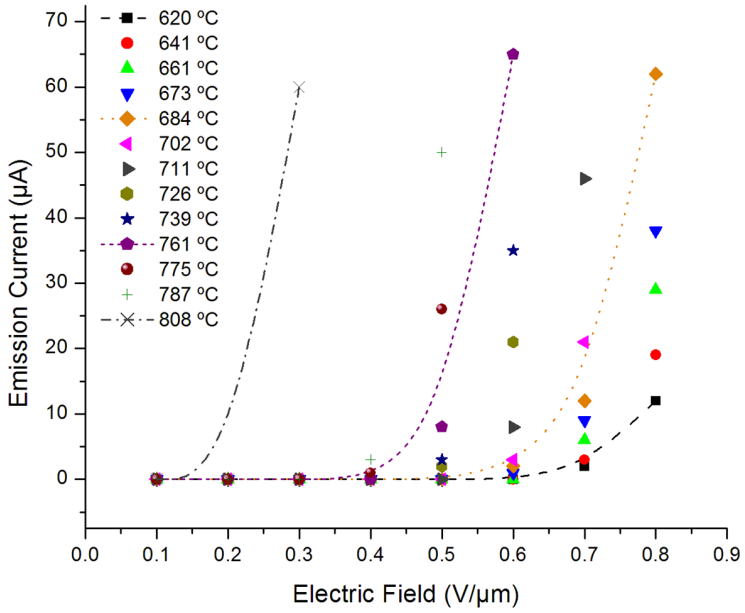

FIGURE 2. Electron Emission from a Sulfur Doped Nanocrystalline Diamond Film at Various Temperatures.

To determine the material properties, the data was fit to the Richardson equation at low electric fields. At an electric

field of 0.5 V/µm a fit to the Richardson equation yields a work function of 2.5 eV and a Richardson constant of 40 A/cm^2 K^2. As the field at the emitter is increased, a shift of the emission current towards higher values is observed. This influence of the field on the emission suggests the use of the field modified Richardson equation, the Schottky relation. With an applied field of 0.8 V/µm at the emitter, a work function of 1.9 eV and Richardson constant of 1 A/cm^2 K^2 is computed. It is evident that a small increase in the electric field results in a significant reduction in the observed work function. The local field at the emitter can be estimated by evaluating the emission barrier lowering due to field enhancement effects. Computed values for the effective work function and Richardson constant at low fields (0.5 V/µm) are used as input parameters for the Schottky formula and a fit is performed to extract the electric field. In Figure 3 the data fit (dashed line) represents a local electric field of about 62 V/µm. At an applied electric field of 0.8 V/µm, this corresponds to a field enhancement factor of β≈78. However, the impact of the electric field on the Richardson constant needs further investigation.

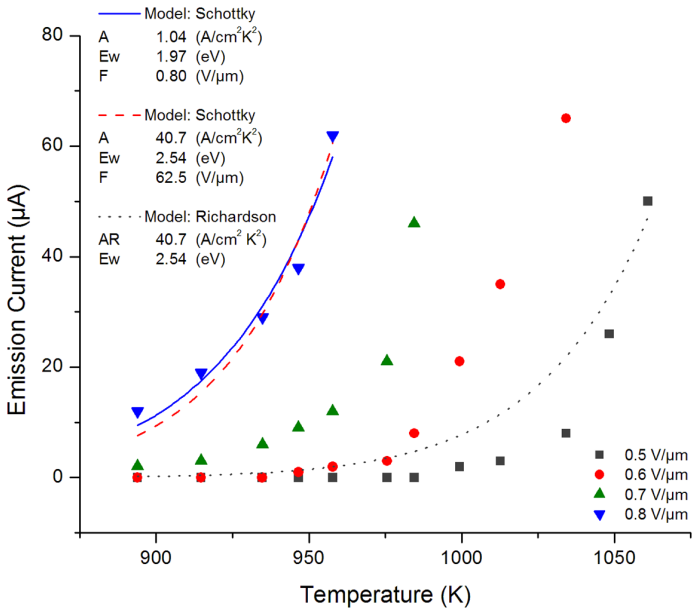

FIGURE 3. Field Enhanced Thermionic Emission from a Sulfur Doped Diamond Film at Various Fields. The Data-Points are Fitted to the Richardson and Schottky Equation (Line).

The emission characteristics from a CNT film do not differ significantly from its nanocrystalline counterpart where the emission exhibits a strong variation in the spatial distribution of the field enhancement factor. As a result, the emission is localized to bright emission sites. For a CNT film, this localization is often attributed to the geometric structure of the nanotube, i.e. a nanometer sized cylinder with high aspect ratio. This in turn corresponds to a high geometric field enhancement factor. Figure 4 depicts the emission characteristic of a carbon nanotube film at various temperatures. The emission current increases with the applied field and at elevated temperatures the threshold field is observed to shift towards lower values.

The observed results indicate that sulfur-doped nanocrystalline diamond and CNT films exhibit similar emission characteristics, but the emission origins may be distinguished based on the field enhancement which can be of an electronic and/or geometric nature. While a proposed band structure for sulfur doped nanocrystalline diamond emphasizes the role of dopants and defects in the thermionic emission component, similar electronic properties have not been established for CNT films.

However, these structures exhibit significant barrier lowering due to an applied field resulting in a reduced effective work function. Moreover, the exact structure of the nanotube, i.e. nanotube body and tip can strongly affect emission properties. For example, simulations have indicated an effective work function ranging from ~1.7 to 5 eV depending on the CNT tip structure. (Chen, Lee and Clark, 2004) Further studies are needed to establish the exact origins of emission for a CNT film. A significant issue is CNT density versus emission site density as direct imaging

techniques estimate up to 10^6 emitting sites / cm^2 for a film composed of ~10^9 nanotubes / cm^2. (Zhang et al., 2004) Similar considerations for nanocrystalline films also need to be addressed.

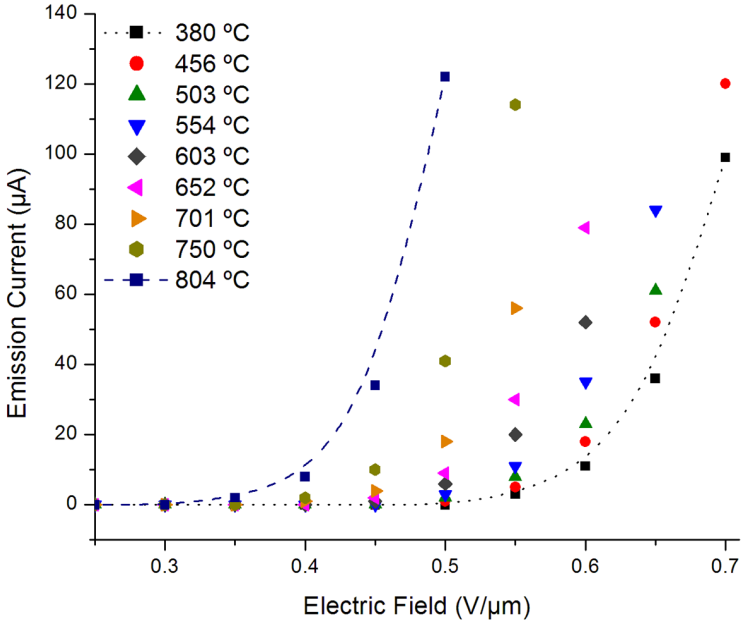

FIGURE 4. Emission Characteristics of a Carbon Nanotube (CNT) Film at Various Temperatures.

CONCLUSIONS

Sulfur doped nanocrystalline diamond and carbon nanotube (CNT) films were synthesized by plasma assisted chemical vapor deposition. These films were characterized for field enhanced thermionic electron emission. The critical material parameters, work function φ and Richardson constant A, were extracted by fitting data to the Richardson and Schottky equation. The work function for sulfur doped nanocrystalline diamond films is significantly altered by the application of an external electric field due to intrinsic field enhancement effects of the material. These induce an enhancement of the local field at the emitting site by a factor of ~78 corresponding to a field of 62 V/μm. As carbon nanotube films exhibit similar emission characteristics, further studies need to address the exact origin for emission. Field enhancement structures can thus prove advantageous in a thermionic converter configuration by providing means to alleviate space charge effects.

NOMENCLATURE

φ = work function (eV)
Φ_E = emitter work function (eV)
Φ_C = collector work function (eV)
A = Richardson's constant ($A/cm^2\ K^2$)
J = emission current density ($A\ cm^{-2}$)
F = electric field ($V\ \mu m^{-1}$)
T = Temperature (K)
$\hbar$ = reduced Planck's constant (J s)
β = field enhancement factor
e = electronic charge (C)
m = electronic mass (kg)
k_B = Boltzmann's constant ($eV\ K^{-1}$)

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