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Sulfur doped nanocrystalline diamond films as field enhancement based thermionic emitters and their role in energy conversion

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Abstract

Sulfur doped nanocrystalline diamond films, like other nanostructured carbon films, exhibit electron emission characterized by a spatial non-uniformity of the field enhancement factor. While field emission effects are observed at room temperature, an increase in emitter temperature is accompanied by an amplified emission current with a simultaneous drop in the threshold field. At low extraction fields a fit of the emission current to the Richardson equation indicates a material work function of ~2.5 eV. The Schottky formula describes thermionic emission at a moderate field and is utilized to determine the work function at an electric field of 0.8 V/μm with a value of ~1.7 eV and a concurrently reduced Richardson constant. This significant difference in the work function of 2.5 and 1.7 eV for 0.5 and 0.8V/μm, respectively can be attributed to field enhancement effects.

Keywords: Doped nanocrystalline diamond; Thermionic emission; Field emission; Energy conversion; CVD

1. Introduction

Thermionic electron emission is the critical phenomenon that describes the motive in the transformation of thermal into electrical energy. A basic vacuum thermionic energy converter is comprised of an electron emitter at an elevated temperature separated by a vacuum gap from a cooler collector. The emission process harnessed in a thermionic energy converter can provide electrical energy without any moving parts making it a highly efficient, low maintenance power source. Early thermionic energy converters based on electron emission from flat metal surfaces suffered from several performance limiting phenomena with space charge the most significant factor. Here, a charge cloud adjacent to the emitter surface impedes successive electrons from traversing the vacuum gap toward the collector. Changes in system design could account for these shortcomings but only at the expense of mobility, operating temperature and materials handling. The most prominent vacuum thermionic energy converter project was developed under the TOPAZ program [1,2].

From the above it is evident, that a reduction in operating temperature and elimination of space charge effects could inspire a new generation of refined vacuum thermionic energy converters in a streamlined configuration suitable for terrestrial and mobile applications. The development of a suitable electron emitter is thus of prime importance.

Efficient electron sources are of ongoing interest due to their wide application range from display devices to spacecraft propulsion systems. However, the major research interest is focused on field emission properties at room temperature from various materials where carbon based emitters are regarded as one of the most promising candidates. Recently, temperature dependent emission studies suggested that doped diamond films would be suitable thermionic electron sources at temperatures <1000 °C [3]. For this material system emission is governed by a negative electron affinity surface in conjunction with dopant/defect states which results in uniform emission characteristics. This is in contrast to emission from other carbon based materials where localized emission, i.e. emission originating from singular sites is observed. The exact mechanism causing localized emission is still widely debated but cannot be confined to a single constituent. However, a non-uniform distribution of the field enhancement factor is fundamental for this emission behavior. It is well known that

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a geometric feature of height, h, and tip radius of curvature, r, exhibits a field enhancement factor proportional to h/r where the electric field is concentrated at the tip of the object from where the emission occurs. Nanostructured carbon materials, i.e. carbon nanotubes (CNTs), nano and ultra-nanocrystalline diamond films exhibit a morphology comprised of a matrix of nanometer size grains separated by a boundary layer which has been argued to be the origin of emission sites [4,5]. The film morphology can thus be described by a conglomerate of structural elements each comprised of a grain and its boundary. However, the high density of these constituents cannot substantiate the orders of magnitude lower emission site density, which is $\sim 10^5/\text{cm}^2$ for a typical nanostructured carbon film. This intrinsic field enhancement based emitter can prove advantageous with respect to space charge effects by providing an accelerated transport of electrons from the emitting surface.

These field enhancement effects play a significant part in the emission behavior. With advances in the development and characterization of nanostructured carbon based materials, novel approaches to thermionic energy conversion could be considered with a goal of simplified operation and the reduction of the operating temperature to well below 1000 °C.

A prime component for a practical thermionic energy converter is an efficient thermionic emitter. The overall performance is governed by the emitter and collector characteristics with a low work function collector preferred for increased power output. It may be assumed that an output open source voltage of 1 V, which would correspond to a work function difference of approximately 1 eV between emitter and collector, should be feasible with current known materials. With an emitter engineered to provide emission current densities of ~ 1 A/cm^2 the total power of the cell could approach or exceed 1 W/cm^2, and an efficiency greater than 20% could be achieved.

In this study we report on the electron emission characteristics for sulfur-doped nanocrystalline diamond films in a parallel plate configuration in a controlled UHV environment at variable emitter temperatures. The objective of this project is to determine the feasibility of sulfur doped nanocrystalline diamond films as electron emitters in a system to directly convert thermal energy to electrical energy at temperatures less than 1000 °C.

2. Experimental

Sulfur doped nanocrystalline diamond films were synthesized by plasma assisted chemical vapor deposition in a 1500 W AsTex IPX3750 reactor. Prior to deposition, the low resistivity silicon (<1 Ω·cm) or polished molybdenum substrates were treated by ultrasonification in a titanium/diamond/ethanol suspension for 30 min, which results in nucleation enhancement for the initial layer [6]. The sulfur source was a mixture of 50 ppm hydrogen-sulfide in hydrogen. Film growth was commenced by controlling gas flow rates of 10–40 sccm for hydrogen-sulfide and 20 sccm for methane. The growth temperature was 900 °C. Typical film thicknesses were between 0.3 and 1 μm as measured by in situ laser reflectance interferometry.

To assess emission characteristics, electron emission microscopy was employed to image in real-time electron discharge from the surface. The instrument, an Elmitec© electron emission microscope operates in a UHV environment and provides a lateral resolution <10 nm. A more detailed discussion of this observation technique can be found elsewhere [7].

3. Results and discussion

Nanocrystalline as well as sulfur-doped nanocrystalline diamond films exhibit similar emission characteristics, i.e. emission from singular sites. The influence of sulfur on the electrical properties of the film is still debated. However, a small incorporation coefficient of $<10^{-6}$ has been reported elsewhere [8]. The same group observed 10–20 ppm of sulfur in films grown with a wide range of H_2S addition. Emission from a typical sulfur-doped nanocrystalline diamond film at room temperature is shown in Fig. 1. Here UV-light from a mercury arc lamp is utilized to image photo-electron emission from the background which appears with uniform brightness in the image. A confined region indicated by the arrow displays emission due to the applied electric field of ~ 5 V/μm. These emitting sites are distributed across the sample with an estimated density of $\sim 10^4/\text{cm}^2$ for a film synthesized with 40 sccm hydrogen-sulfide and 20 sccm methane. The grain like surface morphology exhibits geometric field enhancement at these surface protrusions, which then appear as points with increased brightness as shown in Fig. 1. Here, the surface is irradiated with UV light from a mercury arc lamp and the microscope is focused in the plane of the sample surface. In a previous study, the origin for emission sites from nanocrystalline diamond films was investigated by correlating film morphology with the location of a single emitter. Results indicated that surface structural elements do not exhibit

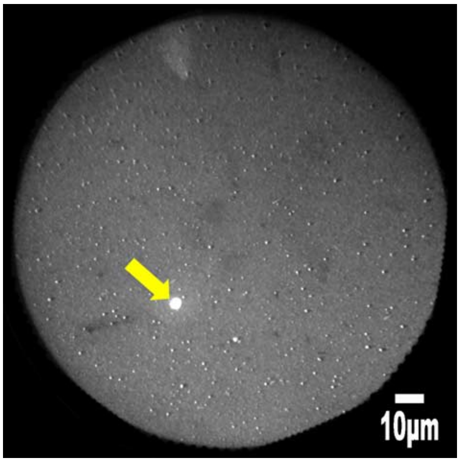

Fig. 1. Electron emission microscopy image of a sulfur doped nanocrystalline diamond film. A single emission site is visible and indicated by the arrow. The image was acquired by irradiating the surface with UV light from a mercury arc lamp.

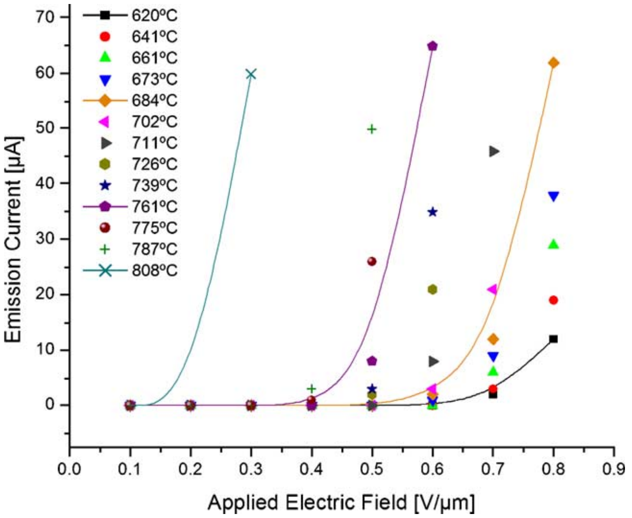

Fig. 2. Electron emission from a sulfur-doped nanocrystalline diamond film at elevated temperatures.

preferred features, which would induce the observed emission behavior, eliminating morphological field enhancement as the sole origin for an emission site [9].

At room-temperature, emission for typical sulfur-doped nanocrystalline films does not significantly differ from emission from undoped nanocrystalline films in threshold field and emission site density. However, at elevated temperatures changes in the emission characteristics were observed. With an increase in sample temperature emission is still confined to the regions emitting at room temperature with no detectable emission from the sample background. This behavior is also shown in current/voltage data plots in Fig. 2. For these measurements the sample was positioned about 1 mm from a metallic electrode, the anode or collector. The temperature of the diamond film was then increased by radiatively heating the substrate.

Current/voltage sweeps were performed at various temperatures. Results in Fig. 2 were acquired from a sulfur-doped nanocrystalline diamond film prepared with 20 sccm hydrogen-sulfide and 20 sccm methane.

The emission data was acquired by increasing the sample temperature from 620 to 808 °C. The threshold field for emission at a temperature of 620 °C is ~0.7 V/μm, and the emission current increases with applied electric field. As the sample temperature is increased, the threshold field for emission is successively diminished. Additionally, with a shift to higher temperature the emission current increases at a higher rate. For classical thermionic emission an emission current can be extracted from the emitter at negligible fields (i.e. at zero field).

Field enhanced thermionic emission as is observed for sulfur-doped nanocrystalline diamond films does not exhibit detectable emission below the threshold field. However, as a first assessment the Richardson equation, which describes thermionic emission at zero field can provide an estimate for material properties with respect to electron emission and it is given by

$$J(T) = AT^2 e^{-\frac{\varphi}{k_\mathrm{B}T}}, \tag{1}$$

where the emission current density J is given by the work function φ, the Richardson constant A, temperature T and Boltzmann's constant k_B. Crucial to the emission are the work function as emission barrier and Richardson's constant as a measure of the emission current density. The data in Fig. 2 can then be evaluated by means of this functionality. Fig. 3 depicts the same data plotted with respect to the Richardson equation where the emission current is displayed as a function of emitter temperature with the applied electric field as parameter. At an applied field of 0.5 V/μm a fit to the dataset provides a work function of 2.5 eV with a Richardson constant of 40 A/cm^2. At higher electric fields a shift in the current/temperature dependency is observed suggesting a fitting approach with a field-modified Richardson equation, the Schottky formula. This relation is given by

$$J(T,E) = AT^2 e^{-\frac{\varphi\sqrt{e^3\cdot E}}{k_\mathrm{B}T}}, \tag{2}$$

where E represents the applied electric field and e the electronic charge. It is evident from [2] that an applied electric field induces a diminished emission barrier, which corresponds to a reduced or effective work function of the material. Performing a fit to the current/temperature dataset acquired at 0.8 V/μm results in a work function of 1.9 eV and a Richardson constant of 1 A/cm^2. This strong reduction in the work function from 2.5 to 1.9 eV can be explained by considering field enhancement effects of the emitter. The Schottky formula in Eq. (2) employs the macroscopic, i.e. applied electric field. Since sulfur-doped nanocrystalline diamond films exhibit an intrinsic field enhancement, this macroscopic field E is enhanced at the location of emission to $\beta\cdot E$, where β is the field enhancement factor.

This locally enhanced field at the emission site can be obtained by evaluating the Schottky formula with a work function from the Richardson fit of 2.5 eV and Richardson's constant of 40 A/cm^2. In order to approximate a work function of 1.9 eV in the fit an electric field of 63 V/μm at the emission

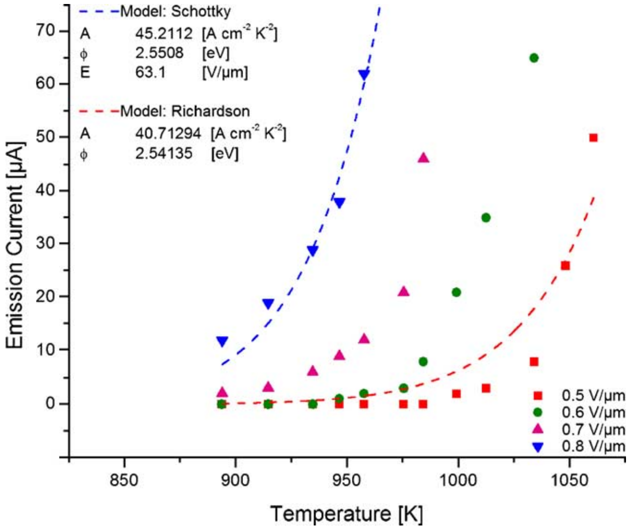

Fig. 3. Electron emission current plotted versus temperature at various fields from sulfur-doped nanocrystalline diamond (the same data as in Fig. 2). The emission data has been fit with respect to the Richardson and Schottky equation to extract the work function of the material.

site is required. Thus, the applied electric field of 0.8 V/μm has been calculated to be enhanced to 63 V/μm, i.e the field is enhanced by a factor of about 78. Field emission at room temperature can be described by the Fowler–Nordheim (FN) functionality

$$J = \frac{1.5 \times 10^{-6} \beta^2 F^2 A}{\varphi} \cdot e^{\frac{10.4}{\varphi}} \cdot e^{\frac{-6.44 \times 10^7 \varphi^{3/2}}{\beta F}}, \tag{3}$$

where work function, φ [eV], field enhancement factor, β, and emission area, A [cm^2], are critical parameters. By measuring the emission current, J [A], as a function of the applied electric field, F [V/cm], the Fowler–Nordheim formula can be evaluated with respect to these three parameters, φ, β and A. However, a simultaneous solution to the FN equation is possible only by estimating values for two parameters where the third can then be computed. It has been shown elsewhere that the field enhancement factor of nanostructured carbon films is typically in the order of several 100 [10,11]. However, these studies were performed by adopting a work function of $\varphi = 5$ eV. Evaluating Eq. (3) with a high work function will then result in a high field enhancement factor. A different group investigated field electron emission from nitrogen doped diamond films at elevated temperatures and determined field enhancement factors <50 with a work function <1.5 eV [12]. These findings are in accordance with our results and indicate the significance of the work function on the field enhancement factor and their correlation.

For a conventional vacuum thermionic energy converter a thermionic voltage of typically 1 V appears across the gap. By adjusting the electrode spacing, the electric field can be controlled to match emission characteristics of the emitter material, i.e. the threshold field for emission.

4. Conclusions

Sulfur doped nanocrystalline diamond films were synthesized by plasma assisted chemical vapor deposition. Electron emission from these films is non-uniform at room temperature. At elevated temperatures emission is confined to singular sites where emission originated at room temperature. Field enhanced thermionic electron emission from sulfur doped nanocrystalline diamond films exhibits diminished threshold fields at elevated temperatures as well as a low effective work function. This emission behavior makes this material prime candidate for vacuum thermionic energy conversion where efficient electron sources are requisite for the transformation of thermal into electrical energy.

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