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On the thermionic emission from nitrogen-doped diamond films with respect to energy conversion

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Abstract

Thermionic energy converters utilize thermal energy and efficiently transform it into more useful electrical energy. A key aspect in thermionic energy conversion is the emission of electrons at elevated temperatures, where the electron emitter is separated from the collector by a vacuum gap and a voltage is generated due to the temperature difference between the emitter and collector. In this study, nitrogen-doped diamond films with a negative electron affinity surface have been synthesized with plasma-assisted chemical vapor deposition, and the electron emission has been imaged using high-resolution electron emission microscopy. This study reports the measurement of a thermovoltage and current, i.e. energy conversion, at temperatures considerably less than 1000 °C.

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

1. Introduction

Conventional thermionic energy conversion is based on electron emission from flat metal surfaces. In its simplest configuration, a thermionic energy converter consists of a hot electron emitter and a cooler collector separated by a vacuum gap. The process is highly efficient, and energy generators based on this concept were constructed and first tested in the late 1960s as the electrical power source for space missions. The most prominent project was developed under the TOPAZ program [1]. Here, the energy generator core was based on flat metal surfaces as the electron emitter, which, in turn, suffered from several disadvantages with respect to design and usability. High temperatures, approaching 1900 K or more, are necessary to provide sufficient emission current from a metallic electrode. For the case of a flat (metallic) emitter surface, a charge buildup will occur outside the corresponding boundary, which will screen other electrons from being efficiently released into vacuum. To obviate these performance-limiting effects, an approach was chosen that resulted in a reduction of the emitter work function and the neutralization of space charge effects by introducing ionizing vapors (typically Cs) into the vacuum gap between emitter and collector [2]. However, this operations approach resulted in a bulky design, and operation was limited to temperatures greater than 1000 °C. Thus, these systems were not deemed suitable for terrestrial and mobile applications.

With advances in the development and characterization of 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. Moreover, the design of a system that does not require an ionizing vapor could result in small, compact devices, which would be appropriate for mobile electrical energy generators.

The electron emission behavior of carbon-based materials includes a wide range of emission characteristics from localized emission sites to uniform emission. Moreover, by introducing dopants, the material can be engineered in such a way that the resulting band structure could lead to efficient electron emission and a reduced effective work function. In

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conjunction with the ability of diamond surfaces to attain negative electron affinity characteristics, a low-temperature thermionic electron emitter could be achieved which could be a key element of a thermionic energy conversion system.

A prime component for a practical thermionic energy converter is an efficient thermionic emitter. However, 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 in first order to a work function difference of 1 eV between emitter and collector, should be feasible with current known materials. With an emitter engineered to provide emission current densities of $\sim$1 A/cm^2, the total power of the cell could approach or exceed 1 W/cm^2.

In this study, results for electron emission of nitrogen-doped diamond surfaces are described, and the surfaces are employed in a vacuum gap emitter system with a variable emitter temperature. The goal of the study is to determine the feasibility of N-doped diamond surfaces as electron emitters in a system to directly convert thermal energy to electrical energy at temperatures less than 1000 °C.

2. Results and discussion

Nitrogen-doped 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 $\Omega \cdot$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. [3] Film growth, after establishing a nucleation layer, was commenced by adjusting gas flow rates from 200 to 437 sccm for hydrogen, from 20 to 2.5 sccm for methane and the addition of 60 sccm of nitrogen. The growth temperature was increased from 600 to 900 °C. It has been reported elsewhere that the doping concentration for high N/C ratios with values up to 40 can be estimated to $\sim 10^{19}$ cm^{-3}. [4] Typical film thicknesses were between 0.3 and 1 μm, as measured by in situ laser reflectance interferometry. A final step included exposure of the film surface to a hydrogen plasma, which would induce a negative electron affinity.

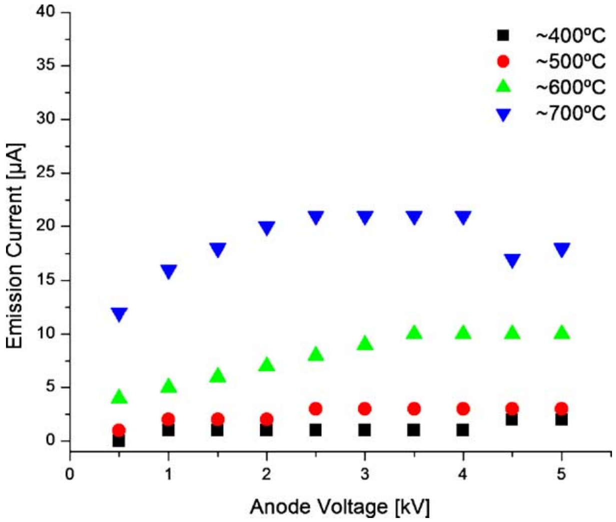

Fig. 2. The temperature dependence of the emission current versus voltage for a Zr-terminated nitrogen-doped diamond film. The emitter-collector distance was 1 mm. At low electric fields, the nearly constant emission indicates a thermionic behavior. The measurements were performed in a UHV system.

Alternatively, NEA characteristics could also be induced on p-type diamond by the deposition of a thin metal layer ($\sim$0.3 nm) of low work function transition metals such as titanium, hafnium or zirconium [5]. Metal deposition was performed by electron beam evaporation at a base pressure of less than 10^{-10} Torr.

Initial measurements included characterization of the electron emission at various temperatures by electron emission microscopy. This technique utilizes an electric field of typically 5 V/μm in its imaging mode and allows observation of changes in the electron emissivity in real time with a lateral resolution of less than 10 nm [6]. Measurements from nitrogen-doped diamond films indicate that electron emission is detectable at temperatures as low as 640 °C with a strong increase in the emission with temperature. It is noteworthy that the emission is uniform unlike the emission from other carbon-based materials. This uniform electron emission behavior shown in Fig. 1 is attributed to the negative electron affinity of the surface [7].

It has been shown elsewhere that operation of N-doped diamond at elevated temperatures results in the degradation

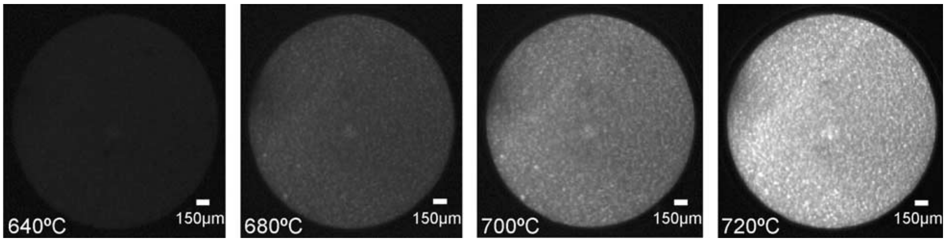

Fig. 1. Electron emission microscopy of hydrogen-terminated, nitrogen-doped diamond surface at various temperatures. The brightness is proportional to the electron emission current.

of the NEA surface characteristic [8]. For hydrogen-induced NEA surfaces, this effect commences at ~800 °C where the emission behavior exhibits a strong reduction in the emission current. Substituting the hydrogen passivation procedure with a Ti termination process allows stable operation of the emitter at temperatures up to 950 °C [8]. The Zr and Hf terminated N-doped diamond films exhibit the same behavior as indicated by our measurements reported here.

Temperature-dependent current/voltage measurements have been performed to characterize electron emission at low electric fields. For thermionic energy conversion, the emission behavior at low electric fields determines the usability of this material as an emitter. An onset of the emission at low temperatures and negligible fields (<0.5 V/μm) are the premises for efficient thermionic energy conversion. Thermionic emission is governed by thermal excitation and the release of electrons from a solid. To prevent a charge buildup adjacent to the emitting surface, an electric field is necessary to prevent this space charge from counteracting emission. An increase in the electric field will result in a constant emission current until a threshold field is approached where field emission processes begin to dominate the total emission behavior. Thus, below a certain threshold field, thermionic electron emission is only defined by the temperature of the emitter. Fig. 2 depicts the current versus voltage at various temperatures for a nitrogen-doped diamond film where a 0.3 nm thick Zr layer was deposited onto the surface to obtain a negative electron affinity and reduced work function. The measurements were obtained in a UHV thermionic emission system.

Thermionic energy conversion measurements were performed in a custom-built characterization system that consists of a heated sample stage (emitter) allowing temperatures up to 1200 °C and a cooled collector mounted on a stage that is moveable in all three spatial directions. Temperatures of the emitter and collector were determined by separate thermocouples, which were calibrated with an optical pyrometer. During a measurement, the emitter is separated by an adjustable distance from the collector, and the emitter temperature is continuously increased. The collector is cooled with flowing gas from a liquid nitrogen dewar allowing an initial collector temperature of <0 °C. During operation at elevated emitter temperatures, the collector temperature increases to about 150 °C.

At elevated temperatures, a self-generated voltage appears across the vacuum gap, i.e. between emitter and collector due to the temperature difference between these two electrodes. This voltage is termed the thermovoltage. By connecting a variable resistive load between emitter and collector, the short-circuit current and open source voltage of the energy conversion cell can be determined.

For our measurements, a metallic collector made of hafnium with a work function of about 3.8 eV was chosen. As the emitter, an ~0.3 μm thick nitrogen-doped diamond film with hydrogen passivation for NEA characteristic was positioned ~100 μm from the collector in a UHV chamber. The temperature of the emitter was then increased and the self-generated thermovoltage, i.e. the open source voltage of the cell, was recorded as shown in Fig. 3. At a temperature of less than 600 °C, a thermovoltage is detectable which increases to 0.23 V at ~750 °C. At an emitter-collector separation of ~80 μm, a current is detectable which indicates thermionic energy conversion.

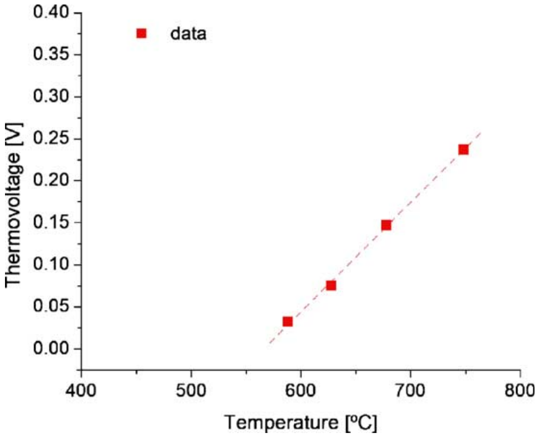

Fig. 3. Thermovoltage as a function of temperature for a nitrogen-doped NEA diamond film (H-terminated) as the emitter and a Hf metal collector separated ~100 μm in a UHV chamber.

3. Conclusion

We have synthesized nitrogen-doped diamond films with NEA surface characteristic induced by hydrogen passivation or metal deposition as the emitter in a thermionic energy conversion system. Electron emission measurements indicate that these films exhibit a lowered effective work function suitable for thermionic emitters. Thermionic energy conversion measurements from nitrogen-doped NEA diamond film emitters and a conventional metal collector indicate the feasibility of energy conversion at temperatures considerably less than 1000 °C.

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