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Low temperature onset for thermionic emitters based on nitrogen incorporated UNCD films

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ABSTRACT

Thermionic electron emission is a key phenomenon utilized in a variety of applications, from communications, space propulsion to direct energy conversion. Doped diamond films with a negative electron affinity (NEA) surface characteristic present a reduced effective work function for electron emission. Our prior research has indicated a work function of ~1.5 eV for nitrogen doped diamond films prepared by microwave plasma CVD. The focus of this study is on the role of the interfacial or nucleation layer. A thermionic emitter was fabricated with a nitrogen incorporated ultra-nanocrystalline diamond (UNCD) nucleation layer and a nitrogen doped diamond surface layer with hydrogen termination. The film exhibited a resistance that decreased with temperature suggesting the role of the dopant, and thermionic electron emission was observed at temperatures < 250 °C. An analysis based on the Richardson–Dushman equation indicated an emission barrier of < 1.3 eV with a Richardson constant of ~0.8 A/cm^2 K^2.

1. Introduction

Vacuum electron emission from a solid can be categorized by field, thermionic and secondary emission where the energy supplied to promote electrons into vacuum is provided by an applied electric field, thermal energy and incident particles, respectively.

Vacuum thermionic electron emission has first been formulated by Richardson and Dushman in their corresponding law expressed by

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

where the total emission current $J(T)$ is a function of the material work function, φ, and the Richardson's constant, A_R, with the emitter at temperature, T, and k_B Boltzmann's constant [1,2]. While the theoretical value of Richardson's constant was determined as 120 A/cm^2 K^2, an experimental evaluation of various materials present a wide range of parameters as shown in Table 1.

Diamond as a wide band-gap semiconductor has long been a preferred candidate for electron emission applications. This is due to the fact of two key characteristics which allow engineering of an emitter with a low effective work function. Exposure of diamond surfaces to a hydrogen plasma establishes hydrogen termination and negative electron affinity (NEA) characteristics where the vacuum level is referenced below the conduction band minimum [3]. For a hydrogen terminated (111) diamond surface the electron affinity, χ, has been reported as −1.2 eV [4]. Similarly, for a hydrogen terminated (100) diamond surface, χ has been measured as −1.3 eV. [5] Identifying suitable n-type dopants would then lead to a surface with a reduced effective work function. The most commonly considered n-type dopant is nitrogen, which is a deep donor with states ~1.7 eV below the conduction band minimum. We have previously reported an effective work function of 1.5–1.9 eV for nitrogen-doped diamond films grown on molybdenum substrates [6]. In contrast, for nitrogen-doped single crystal diamond, photoemission measurements indicate strong upward bend-bending and a much larger work function of ~3 eV [7]. Apparently the sp^2 bonding in the nitrogen-doped CVD diamond films affects the surface properties of the material leading to reduced band bending and a low effective work function. In fact, measurements from our group have indicated that as the temperature is increased, the work function decreases. This effect was attributed to either or both a reduced band bending or a change in the Fermi energy due to electrons populating the conduction band.

The focus of this study is on the role of the nitrogen-incorporated UNCD interfacial layer between the metallic substrate and the nitrogen-doped diamond top layer. For efficient thermionic emission this layer must have a low contact resistance and a low resistivity. Previous results have established that nitrogen incorporated into the growth of ultra nanocrystalline diamond (UNCD) resulted in films with n-type character and low resistivity [8]. It has been suggested that nitrogen in the grain boundaries and in the grains both contribute to the electrical conductivity. In this study we establish that the UNCD films result in an ohmic contact to the nitrogen-doped diamond top layer and a resistance that decreases with temperature. Moreover, the films show thermionic emission characteristics with a decreased work function.

2. Experimental

Sample preparation included ultrasonic abrasion of metallic substrates in a nanodiamond-dimethyl sulfoxide (DMSO) suspension for

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Table 1
Work function and Richardson's constant *A* for various materials displaying a significant deviation from the theoretical value of 120 A/cm^2 K^2

Material	Richardson A_R [A/cm^2 K^2]	Work function [eV]
W	74	4.5
Mo	55	4.1
Re	200	5.1
Graphite	48	4.8

30–60 min. This was followed by a rinse in methanol and drying with nitrogen gas. Growth of the emitter structure was comprised of a step process initiating a nitrogen incorporated UNCD layer under the addition of argon, nitrogen and methane in a 900 W microwave plasma at 20 Torr chamber pressure and a substrate temperature of ~800 °C. Nucleation and film thickness were monitored in situ by laser reflectance interferometry (LRI). After the UNCD layer with desired thickness of ~400 nm was established, parameters were adjusted for nitrogen doped diamond growth. Microwave power and chamber pressure were increased to 1300 W and 50 Torr, respectively. Hydrogen flow was established at 400 sccm with a reduction of methane flow to 2 sccm. Film thickness was 100–200 nm as determined by LRI evaluation. Exposure of the final film surface to a hydrogen plasma resulted in an NEA surface characteristic.

For temperature dependent resistivity measurements gold contacts were deposited on the clean surface in UHV by electron-beam evaporation. Thermionic emission characterization was performed in a specially designed UHV test and measurement system with a base pressure $<5\times10^{-10}$ Torr. The apparatus included an anode moveable in all 3 spatial directions and a radiatively heated sample stage capable of temperatures up to 1200 °C. Temperature readings were recorded employing a 2-color pyrometer. Electron emission current and applied bias were controlled by a Stanford Research I/V source and measure unit.

3. Results and discussion

Preparing an efficient electron emitter relies on a structure with low cross plane resistivity. In our approach we present an emitter configuration based on a metallic substrate (molybdenum), a nitrogen-incorporated UNCD nucleation layer, and a nitrogen-doped, hydrogen terminated diamond top layer. The new component in this structure is the nitrogen-incorporated UNCD layer, which is proposed to provide a junction with a low contact resistance to the substrate as well as low film resistivity that does not limit the electron emission. In this section we report first the surface morphology and comment on the sp^2 bonding in the film, then describe the resistivity results, and finally, we present the thermionic emission results.

Fig. 1 presents an electron microscope scan of a nitrogen-incorporated UNCD film. An estimate of the ratio of sp^2 and sp^3 bonded carbon can be obtained by evaluating the film morphology. Assuming sp^3 bonded carbon grains and sp^2 bonded carbon grain boundaries would present a ~35% sp^2 bonded carbon fraction in the film. This high fraction of sp^2 bonded carbon may contribute to the conducting nature of the UNCD nucleation layer.

The temperature dependence of the cross plane resistivity of the UNCD/N-doped diamond emitter structure is shown in Fig. 2. It is notable that the current–voltage dependence is linear (ohmic) over the measured range. At an emitter temperature of 100 °C the cross plane resistivity was measured with a value $\rho=2.5\times10^3$ Ω cm. Increasing the emitter temperature to 400 °C resulted in a drop in resistivity to $\rho=0.7\times10^3$ Ω cm. These results are consistent with n-type character of the film where the carrier concentration in the film increases as a function of temperature. The measured resistance includes effects due to the Schottky barrier at the interface and to the resistance of the film. For a film with a 1% nitrogen content a resistivity of ~60 Ω cm at room temperature has been reported elsewhere [9].

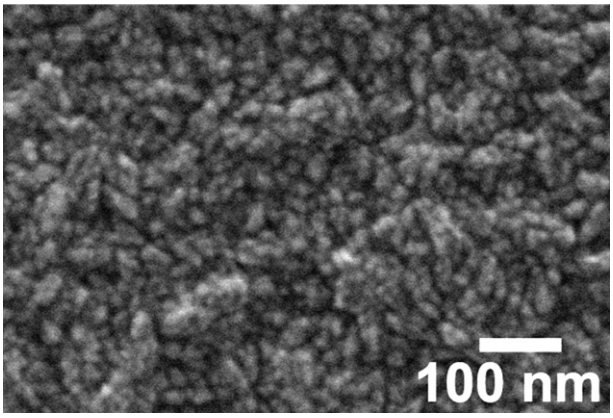

Fig. 1. Scanning electron microscope image of a nitrogen-incorporated UNCD film used as a low resistivity nucleation layer.

Crucial to electron emitter performance is a low resistivity substrate material, which is stable at elevated temperatures. In addition, the materials' carbide must also exhibit high conductivity as it may potentially form at the substrate interface. Molybdenum as a refractory metal exhibits high temperature stability and forms a carbide with a low resistivity on the order of 100 μΩ cm compared to 100–200 Ω cm for silicon carbide. Considering the possibility of interface reactions during film growth is crucial because of the high temperatures (~800 °C) and reactive carbon-rich environment. Our measured results do not appear to reflect a resistance instability or an increase in resistance due to the interface reactions.

Thermionic electron emission (Fig. 3) was obtained as a function of temperature from 523 K up to 700 K from the UNCD/N-doped diamond emitter structure. Electron emission from this structure exhibited a detectable emission of 90 nA at temperatures <250 °C. The data was fit to the Richardson–Dushman relation, and as presented in Fig. 3 the results are consistent over the measured temperature range. Based on the fitting an effective work function of 1.29 eV is obtained with an emission constant of 0.84 A/cm^2 K^2. To our knowledge this is the lowest work function reported for N-doped diamond. The emission appears stable over a time period of hours, and the emission constant is significantly reduced from the value of 120 A/cm^2 K^2 predicted for metallic surfaces.

There are several important points to be discussed with respect to this data. At first there is need to address whether the N-doped UNCD results in an improvement over previous films that did not include this layer. It is evident that these structures exhibit more intense emission at

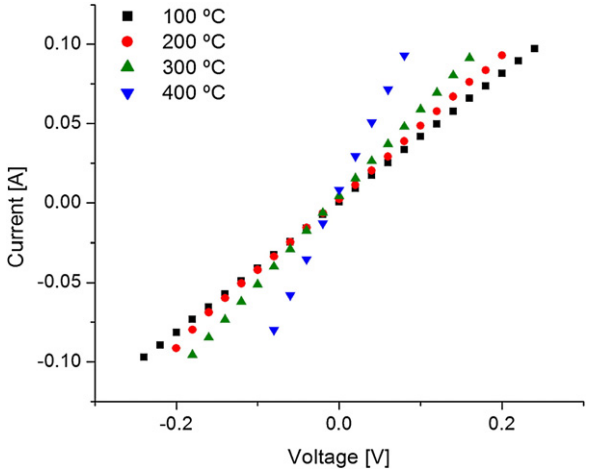

Fig. 2. Temperature dependent cross-plane resistivity of a thermionic emitter structure based on a metallic substrate, a nitrogen-incorporated UNCD nucleation interfacial layer and a nitrogen-doped diamond top layer.

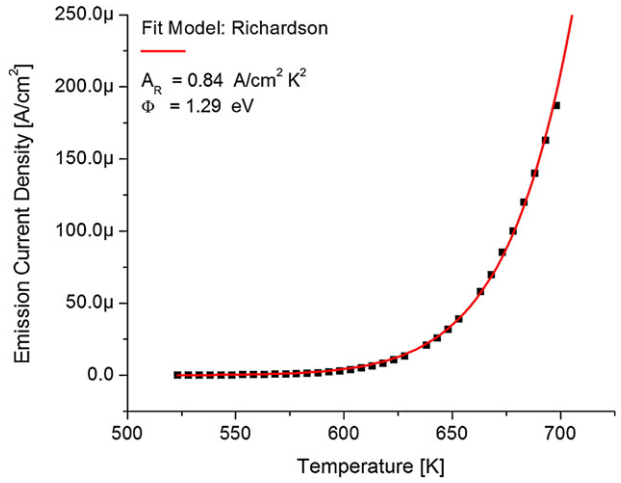

Fig. 3. Thermionic emission data (squares) and data-fit (line) to the Richardson–Dushman equation from a thermionic emitter structure based on a molybdenum substrate, a nitrogen-incorporated UNCD nucleation interfacial layer, and a nitrogen-doped, hydrogen terminated diamond top layer.

lower temperatures than any of the N-doped films produced in previous studies in our laboratory [10]. In a related study on high-temperature electron field emission from nitrogen-doped CVD diamond films a work function of 2.26 eV at 500 °C was reported [11].

Secondly, the aspect whether the N-doped UNCD layer effects the characteristics of the thermionic emission beyond just a reduction of the resistance needs to be identified. Evidently, the layer also affects the work function of the structure. The work function is clearly dependent on two aspects, the band bending and the position of the Fermi level in the band gap. These two effects become interrelated at some level and difficult to separate. It seems evident that the N-doped UNCD results in a film with an increased carrier concentration which could affect both the band bending and the Fermi level position. The usual picture for a doped semiconductor is that the density of electrons in the conduction band at any temperature is determined by the doping density. However, in this case because of the low resistivity contact and the thin diamond layers, electrons can be supplied from the metallic substrate, which results in a much higher carrier concentration than would be expected from the suggested doping density.

However, the theoretical value for the Richardson's constant of 120 A/cm^2 K^2 predicted for metallic surfaces is significantly reduced to 0.84 A/cm^2 K^2. The role of the semiconductor density of states and effective mass has not been properly accounted for in this analysis, but it is evident that the reduction in the resistance due to the UNCD interfacial layer has enhanced the emission intensity.

In contrast, from our previous studies which employed nanocrystalline (NCD) interfacial layers, as opposed to nitrogen-incorporated ultra-nanocrystalline (UNCD) interfacial layers, the films showed a resistance across the film of ~MΩ with higher thresholds for thermionic emission and reduced overall emission intensity at any applied voltage [12]. It is evident that the nitrogen incorporated UNCD interfacial layers can provide the low resistivity necessary for an efficient emitter structure with reported n-type conductivity and bulk carrier concentration up to 10^{21}/cm^3 [13–15]. Conductivity in these films has been ascribed to the preferred incorporation of nitrogen into the high density grain boundary matrix [16,17].

4. Conclusion

We have synthesized an emitter structure that is based on a nitrogen-incorporated UNCD interfacial layer with a nitrogen-doped, hydrogen terminated diamond surface layer on a metallic substrate. Nitrogen incorporated into grain boundaries and diamond domains results in a low contact resistance and a low resistivity UNCD nucleation layer which significantly improves emitter performance. With a highly nitrogen-doped, hydrogen terminated NEA diamond top layer a low effective work function of 1.29 eV has been deduced from thermionic emission data. Thermionic electron emission from this UNCD based structure commences at temperatures <250 °C. This novel approach to thermionic emission based on semiconductors could significantly reduce power requirements for conventional thermionic electron sources. Further improvements which could lower the resistance of the structure could result in additional improvements in the thermionic operation of these structures.

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