



Field enhanced thermionic electron emission from sulfur doped nanocrystalline diamond films

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Abstract

Thermal activation of field enhancement based emitters can provide efficient means of lowering the emission barrier, thus enabling high current density electron sources. Microwave plasma assisted chemical vapour deposition was employed to synthesize sulfur doped nanocrystalline diamond films with various sulfur/carbon concentrations. Electron emission at elevated temperatures was characterized by direct imaging of the emission utilizing electron emission microscopy. Sulfur doped nanocrystalline diamond films exhibit electron emission from singular sites indicating a non-uniform distribution of the local field enhancement. The threshold field for electron emission changes significantly by varying the sulfur/carbon concentration in the gas phase. At elevated temperatures the emission is strongly enhanced but remains confined to the intense emission sites.

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1. Introduction

Nanostructured carbon materials, i.e. nanocrystalline and carbon nanotube films can be described as field enhancement based electron emitters. Electron emission from these films is characterized by a localized discharge of carriers from the surface [1]. This non-uniform emission can prove to be advantageous in conjunction with a thermionic energy conversion configuration if thermionic effects in the emission characteristics are superimposed on the emissivity. The concept of thermionic energy conversion, per se, is the transformation of heat into electrical energy by combining a hot emitter separated by a vacuum gap from a cooler collector. Electron emission from a flat surface may be limited by space charge effects where electrons released from the emitter screen the electric field for successive carrier emission. We are proposing that this reduction in the emission current and thus performance limiting effect may be overcome by employing field enhancement based structures. Moreover, the field

enhancement effects incorporated into thermionic emitters could allow the design of novel thermionic energy converters with the potential of highly efficient operation at temperatures less than 1000 °C.

In general, electron emitters can be characterized by the predominant electron extraction mechanisms, i.e. thermal and field induced processes. Consequently, their emission can be described with the Richardson–Dushman or Fowler–Nordheim relations. For thermionic emission the Richardson–Dushman equation is

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

with the Richardson constant

$$A_R = \frac{emk_B^2}{2\pi^2\hbar^3}$$

For field emission the Fowler–Nordheim equation is

$$J(E) = AE^2 e^{-\frac{B\phi^{3/2}}{E}} \quad (2)$$

with the constants

$$A = \frac{e^3}{16\pi^2\hbar\phi t^2 \left(\frac{\sqrt{e^3 E}}{\phi}\right)}$$

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and

$$B = \frac{4}{3e} \left(\frac{2m}{\hbar^2} \right)^{1/2} v \left(\frac{\sqrt{e^3 E}}{\phi} \right),$$

where $t(y)$ and $v(y)$ are tabulated functions [2].

It is evident from Eqs. (1) and (2) that temperature, T , and electric field, E , are critical variables in Richardson–Dushman and Fowler–Nordheim emission, respectively. For both relations the emission barrier is dependent on the work function, ϕ , of the material. Increased electron emission can thus be achieved by lowering the value of this emission critical parameter. The high work function often associated with carbon based materials, of the order of 5 eV, can be a limiting factor for electron emission applications. However, adjustments in the electronic and film structure can give rise to a considerably lower actual or effective work function. We have shown in a previous study that nitrogen doped diamond films exhibit strong temperature dependence to the emission with significant emission detected at ~ 700 °C [3].

An efficient thermionic electron source can thus be engineered by introducing donor states within the crystal lattice, which in turn results in a reduced work function of the diamond film. We have also previously reported efficient field emission from S-doped diamond films and we have suggested that sulfur states contribute to the observed thermionic emission behavior [1]. Although the exact role of this impurity is still under investigation, results from electron emission measurements of sulfur doped nanocrystalline diamond films indicate diminished threshold fields for field emission at room temperature [4,5]. The same group derived n-type characteristics from electrical conductivity measurements with 1–2 free negative charge carriers per 100 sulfur atoms [6]. Field emission properties can also be strongly influenced by film morphology, where changes in the threshold field can be attributed to sp^2 and sp^3 bonding ratio, grain size and shape and film thickness [7].

Our experiments showed an intriguing difference between the emission from the S-doped and N-doped films. The electron emission from the N-doped diamond films displayed relatively uniform emission from the surface, while the S-doped film displayed localized intense emission sites typical of that observed in nanocrystalline diamond [8]. It has been suggested that localized emission is an indication of field enhancement.

The effect of field enhancement on the field emission from diamond and carbon films has been the subject of numerous studies. However, field enhancement will also affect thermionic emission. The effect is a reduction in the barrier, which has been described by Schottky, and results in a modification of the Richardson–Dushman equation [9]:

$$J(E, T) = A_R T^2 e^{-\frac{\phi - \sqrt{e^3 E}}{k_B T}}. \quad (3)$$

Here, the effective work function corresponds to the work function, ϕ , minus a term, $\sqrt{e^3 E}$, which is dependent on the electric field, E .

In this paper we report on the thermionic electron emission characteristics from sulfur doped nanocrystalline diamond films with an emphasis on barrier lowering caused by field enhancement effects. Our approach is two-fold. We employ electron emission microscopy at elevated sample temperatures to determine whether the emission is characterized by local emission sites throughout the temperature range, and we record temperature dependent current–voltage curves to quantify the emission characteristics of the materials. In this study we employ two different gas phase ratios for the S-doped films.

2. Experiments

Sulfur doped nanocrystalline diamond films were synthesized by plasma assisted chemical vapour deposition in an Astex© IPX3500 1500W reactor with an RF induction-heated graphite susceptor. Gas delivery is regulated by mass flow controllers. The deposition system employs laser reflectance interferometry (LRI) for in situ monitoring of the film growth. Process gases were 50 ppm hydrogensulfide in hydrogen as dopant source and 100% methane as the carbon source.

The substrate material was 1 in. diameter polished molybdenum with a thickness of 1 mm and low resistivity ($< 0.5 \Omega \text{ cm}$) Si (100). Pre-treatment included a 30 min ultrasonic abrasion in a diamond/titanium/ethanol suspension utilizing $< 1 \mu\text{m}$ diamond and $35 \mu\text{m}$ titanium powder. A rinse with methanol and drying the substrate with nitrogen gas concluded the pre-treatment process. This procedure has been shown to enhance nucleation and is described in more detail elsewhere [10].

We have examined two sets of sulfur doped nanocrystalline diamond films with different sulfur–carbon ratios in the gas phase. Common processing parameters were ~ 830 °C substrate temperature, 900 W microwave power and 20 torr chamber pressure. The first set was prepared by using 180 sccm $\text{H}_2\text{S}/\text{H}_2$ and 20 sccm CH_4 which corresponds to $[\text{S}]/[\text{C}] = 0.0045$ while flow rates for the second set were 60 sccm $\text{H}_2\text{S}/\text{H}_2$ and 20 sccm CH_4 resulting in $[\text{S}]/[\text{C}] = 0.0015$, accordingly. Final film thickness for both samples was $\sim 0.3 \mu\text{m}$ after a 2 h deposition period. Sample growth was terminated by simultaneously shutting down the microwave plasma, RF heater and gas flows, and a cool down to room temperature. Sample transfer was initiated by venting of the reactor chamber with argon.

For a comprehensive emission characterization, electron emission microscopy was utilized for direct imaging of the spatial emission distribution. The instrument, an Elmitec© electron emission microscope, operates in a UHV environment with a lateral resolution less than 10 nm. With a radiatively and e-beam heated sample stage, thermionic

excitation up to 1200 °C is feasible in addition to photo-excitation with light from a mercury arc lamp. An electric field, typically ~ 5 V/ μm between sample and anode, is utilized to accelerate emitted electrons through an electromagnetic lens column which provides electron-optical magnification, image formation, and projection onto a phosphor screen [11].

In a separate experimental system, current–voltage scans at various temperatures complemented the emission characterization. The measurements were performed in a custom built UHV thermionic emission measurement system with a base pressure less than 2×10^{-10} torr. In this system, a metallic anode, moveable in all three spatial directions, is positioned typically 100 μm from the sample surface. Nitrogen gas from a liquid nitrogen dewar is utilized as a coolant to control the anode temperature, which approaches 150 °C during a measurement cycle where the emitter temperature is increased to about 1000 °C. The radiatively heated sample stage allows emitter temperatures up to 1200 °C. Current–voltage data acquisition was performed utilizing a Stanford Research PS350 power supply. Data acquisition in a UHV environment ensured surface integrity of the nanocrystalline diamond films.

3. Results

Temperature dependent electron emission measurements performed in an electron emission microscope were utilized to image emission from singular sites at various temperatures. Samples for imaging in the microscope were grown on low resistivity (< 0.5 Ω cm) Si (100) substrates with [S]/[C]=0.0015. To determine the dependence on temperature, a region of the sample was imaged which displayed a single emission site. Fig. 1 depicts a set of electron emission microscope images obtained with the sample at elevated temperatures. The two left images in Fig. 1(a) and (b) were acquired by irradiating the surface with UV light and the resulting images include a contribution from UV photo-excitation. In the absence of photoemission, field enhanced thermionic emission is the sole contributor to the emission image as shown in Fig. 1(c). The first aspect that is evident

from the images is that the emission is largely due to single emission sites, and this is true even at elevated temperature. Compared to the emission site density of $\sim 10^4/\text{cm}^2$ for intrinsic nanocrystalline diamond films, this sulfur doped nanocrystalline film exhibits a considerably lower emission site density. From the images, it is apparent that the emission intensity from the bright site increases as the temperature is increased. The temperature was cycled up and down (400–750 °C) several times and the emission intensity apparently followed the temperature with no evident degradation. The images display the intensity of the emission with and without photo excitation. The intensity of the bright emission site appears to be independent of the UV photoexcitation, while the uniform emission from the surface is only detectable when the UV photoexcitation is present.

Samples for I/V measurements were grown on polished molybdenum substrates. To quantify the emission, current/voltage measurements were performed in a separate UHV system and the emission current was recorded as a function of applied potential and temperature. Fig. 2 presents the emission behavior for the doped nanocrystalline diamond films with different sulfur–carbon gas phase ratios. Films with [S]/[C]=0.0045 as shown in Fig. 2(a) exhibit a moderate temperature dependence in the emission and a small drop in the threshold field at higher temperatures. However, at electric fields > 1.7 V/ μm a variation in temperature results in a more pronounced change in the emission current.

At gas phase ratios [S]/[C]=0.0015 the overall emission behavior changes significantly. One significant result is the observation of a diminished threshold field shifted ~ 0.75 V/ μm to lower values. In addition, the temperature dependence of the emission current becomes more distinct resulting in well separated, individual I/V curves. Concurrently, the field induced emission current increases at higher rates as the emitter temperature is increased.

4. Discussion

Non-uniformity in the emission is often considered as an indication that the spatial distribution of the electric

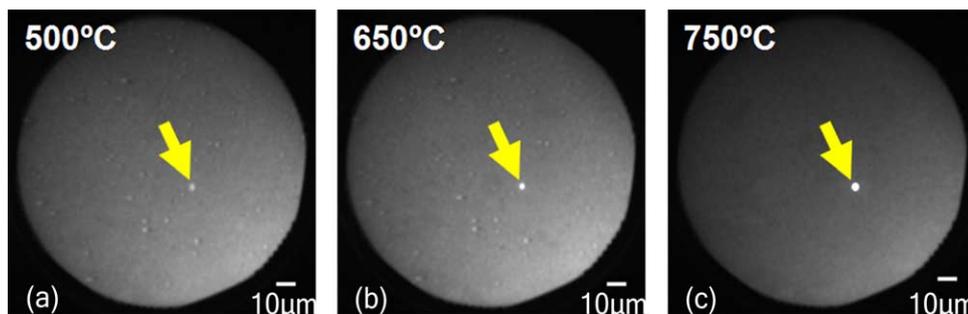


Fig. 1. Electron emission microscopy of sulfur doped nanocrystalline diamond on Si (100) at (a) 500 °C under UV light irradiation, (b) at 650 °C under UV light irradiation and (c) at 750 °C without photo excitation. The electric field for all three images is 5 V/ μm .

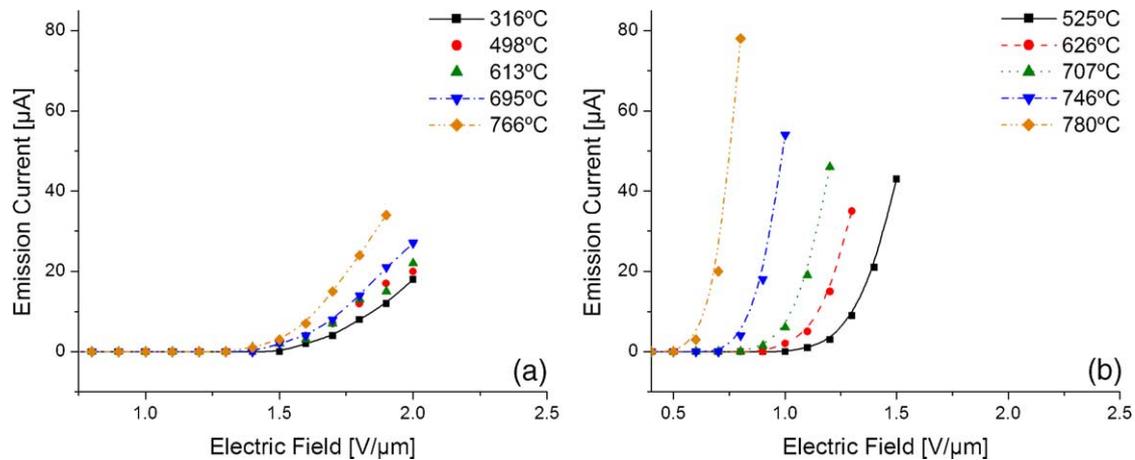


Fig. 2. Electric field dependent thermionic electron emission from sulfur doped nanocrystalline diamond films with (a) gas phase ratio $[S]/[C]=0.0045$ and (b) $[S]/[C]=0.0015$.

field at the surface is non-uniform. These characteristics have been ascribed to variations in surface morphology or conductivity and can be described by the field enhancement factor. The observation of bright emission sites is typical for nanocrystalline diamond films, however, the detailed origin of the bright, localized emission is still debated. We have previously reported that undoped nanocrystalline diamond films exhibit a weak temperature dependence of the electron emission up to 1000 °C [1].

The observation of a strong temperature dependence of the emission from these materials suggests that the incorporation of sulfur into the nanocrystalline structure contributes states, which enhance the emission. The presence of bright emission sites also indicates a high β in some regions of the sample. Moderate temperature activation at low electric fields suggests shallow states, which can supply electrons to the emission current. The defect states associated with the nanocrystalline diamond can then contribute to the total emission by providing conduction paths and field enhancement. Increasing the temperature will cause these states to become populated and tunnelling into vacuum can occur at lower electric fields resulting in a reduced effective work function and, consequently, in the observed temperature dependence.

We note that we have observed a change in the threshold field for films synthesized with different sulfur/carbon concentration ratios in the gas phase indicating that the film properties significantly affect the emission process. We are suggesting that two aspects contribute to the observed temperature dependent emission: additional electronic states and field enhanced sites from the nanocrystalline material. Since our sample with more sulfur showed a lower temperature dependent emission, we are led to conclude that the nanocrystalline structure of the film is also significant in enhancing the emission from the doped films. It is evident that more extensive research is necessary to verify these suppositions and to establish

the relative benefit of doping and nanocrystalline film structure.

5. Conclusion

We have synthesized sulfur doped nanocrystalline diamond films by plasma assisted chemical vapour deposition. Thermionic field emission results indicate electron emission originating from singular sites at all temperatures and the emission increases with temperature. The temperature dependence of the emission current vs. voltage indicates significant electron emission at electric fields of ~ 1 V/ μm . We suggest that the emission is due to both the structure of the nanocrystalline films and the effects due to S-doping. The observed emission characteristics, which include field enhancement in conjunction with a strong thermionic component, make this material a prime candidate for an emitter in a thermionic energy conversion configuration where the field enhancement could reduce space charge limiting phenomena.

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