

特集 Thermionic Electron Emission from Nitrogen Doped Homoepitaxial Diamond with Respect to Energy Conversion*

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Nitrogen-doped homoepitaxial diamond films were synthesized for application as thermionic energy conversion. Thermionic electron emission measurements were conducted where the emission current was recorded as a function of emitter temperature. At a temperature $< 600^{\circ}\text{C}$ an emission current was detected which increased with temperature, and the emission current density was about $1.2\text{mA}/\text{cm}^2$ at 740°C . The electron emission was imaged with photoelectron emission microscopy (PEEM) and thermionic field-emission electron microscopy (T-FEEM). The image displayed uniform electron emission over the whole surface area. Thermionic emission and ultraviolet photoemission spectroscopy were employed to determine the temperature dependent electron emission energy distribution from the nitrogen-doped homoepitaxial diamond films. The photoemission spectra indicated an effective work function of 2.4eV at 550°C . These values indicate reduced band bending and establish the potential for efficient electron emission devices based on nitrogen-doped homoepitaxial diamond.

Key words : Diamond, Thermionic emission, Energy conversion, Nitrogen doped, Homoepitaxial

1. INTRODUCTION

Energy conversion based on vacuum thermionic emission has been explored for many years and prototype systems have been developed and tested¹⁾. A schematic diagram is given in Fig. 1. The operation is based on the thermionic emission of electrons from a hot surface and the collection of the electrons at a cooler collector. The emitter and collector are separated by a small vacuum gap. Since the thermionic emission involves hot electrons, these electrons carry excess energy which can be converted into electrical power. The operation can be described in a motive diagram as shown in Fig. 2¹⁾. In this diagram the operation is in a regime where space charge effects can be neglected. As indicated in the schematic, the barrier to emission is the work function of the emitter material, an electric potential V will develop at the cooler collector which can provide power to the electrical circuit. The advantage of this approach is that the vacuum blocks thermal transport by phonons although radiative losses must be considered, and the barrier effectively selects hot electrons which leads to a high conversion efficiency. Thus conversion efficiencies greater than 20% can be achieved.

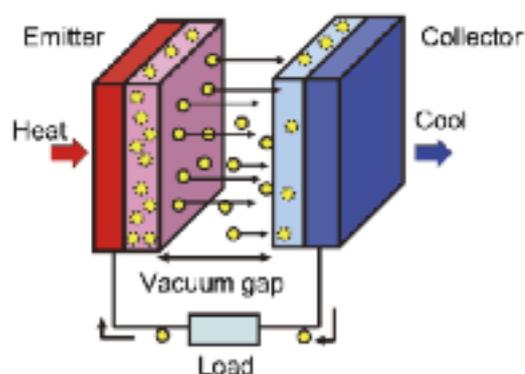


Fig. 1 Schematic diagram of thermionic energy conversion

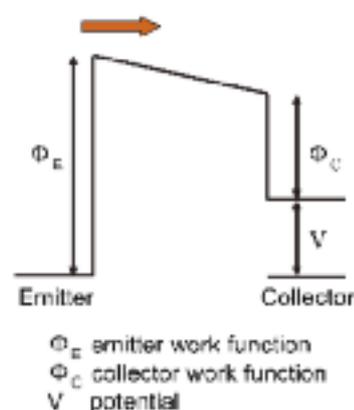


Fig. 2 Motive diagram of thermionic energy conversion under the ideal mode operation

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The disadvantages are that since the work functions of most materials are greater than 3eV, emitter temperatures greater than 1000°C are required to achieve significant energy densities greater than 1W/cm². Thus, the primary goal of the research has been to explore new materials that would exhibit low work functions to enable operation at less than 1000°C. Nitrogen doped diamond is considered to be one of the most attractive materials for low temperature thermionic electron emission because the diamond surface shows a negative electron affinity, and the N impurities act as electron donors²⁾³⁾⁴⁾. This means that electrons excited into the conduction band could be emitted into a vacuum with no barrier. A schematic and short description is shown in Fig. 3. In previous studies, nitrogen-doped polycrystalline diamond films showed thermionic electron emission at temperatures less than 400°C. The results exhibited a low work function in the range of 1.5-1.9eV and an increased performance of thermionic electron emission⁵⁾⁶⁾. However, problems related to the polycrystallinity of the film still remain and limit further understanding of the electron emission properties. Thus, it is necessary to study the electron emission properties of nitrogen-doped diamond without the effects of surface roughness and inhomogeneity due to grain boundaries.

This study focuses on the thermionic electron emission from nitrogen doped single crystal diamond to exclude the above problems. Previously, nitrogen-doped, type-Ib diamond crystals with (001)-oriented surfaces were studied and the amount of upward band bending has been estimated to be ~1.7eV which would increase the work function of the material and raise the emission barrier⁷⁾. In this study, we report the observation of thermionic electron emission from nitrogen-doped homoepitaxial diamond films at a temperature of less than 600°C and discuss the relationship of the thermionic electron emission and the surface electronic properties.

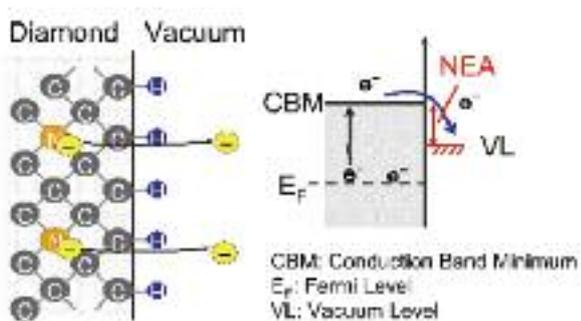


Fig. 3 Rationale of n-type diamond thermionic emitter

Table 1 Growth conditions for nitrogen-doped homoepitaxial diamond

| | |
|--------------------------------------|---|
| Source Gases | H ₂ , CH ₄ , N ₂ |
| [CH ₄]/[H ₂] | 0.05% |
| [N]/[C] | 20 |
| Pressure | 50Torr |
| Substrate Temperature | ~800°C |
| MW Plasma Power | 1300W |
| Substrate | I b, (001) |

2. EXPERIMENTAL

Nitrogen-doped homoepitaxial diamond films were synthesized by plasma assisted chemical vapor deposition. Substrates used were 3x3mm² commercially available high-temperature high-pressure (HTHP) type-Ib diamond crystals with (001)-oriented surfaces. The epitaxial layer growth conditions are summarized in Table 1. The source gas was 0.05% CH₄ diluted with H₂ (CH₄/H₂). Nitrogen gas was used as a dopant gas for nitrogen doping. The parameters of gas pressure, substrate temperature, and microwave power were 50Torr, 800°C, and 1300W, respectively. The incorporation of nitrogen in the films was evaluated by secondary-ion mass spectroscopy (SIMS) and it was ~4x10¹⁹cm⁻³. The nitrogen concentration was quantified using implanted standard samples. Film morphology and sp² concentration were characterized using an atomic force microscopy (AFM) and Raman spectroscopy with 532nm excitation.

Thermionic electron emission measurements were conducted in an UHV environment with a base pressure < 5x10⁻¹⁰ Torr, and the emission current was recorded as a function of emitter temperature. 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.

Photoelectron emission microscopy (PEEM) and thermionic field emission electron microscopy (TFEEM) measurements were carried out to evaluate the uniformity of the electron emission.

The spectrum of the electron emission of N-doped diamond films was characterized with temperature dependent UV-photoemission spectroscopy (UPS) and thermionic emission spectroscopy (TES). The measurements were carried out in a UHV chamber with a base pressure of 5x10⁻¹⁰

Torr. Ultraviolet photoelectron spectra were obtained with HeI (21.2eV) radiation, and the spectrum of the emitted electrons was measured with a VSW-HA50 hemispherical analyzer operating at a resolution of 0.1eV. Thermionic emission spectra can be obtained with the same electron analyzer and sample configuration simply by shutting off the UV excitation. The temperature range of the measurements was limited to 600°C.

3. RESULTS AND DISCUSSION

Fig. 4 shows a typical surface morphology of nitrogen doped diamond films grown on a Ib substrate. Non-epitaxial crystallites and pyramidal hillocks, which are often observed on (001) homoepitaxial CVD diamond, were detected^{8) 9) 10)}. Fig. 5 shows the image observed by AFM. Step bunching along a specific crystal orientation is observed. The entire surface is covered with steps, and the height of these steps was estimated at between 10 and 20 nm. Step bunching was suggested to be evidence for step-flow growth in (001) homoepitaxial diamond growth^{11) 12)}.

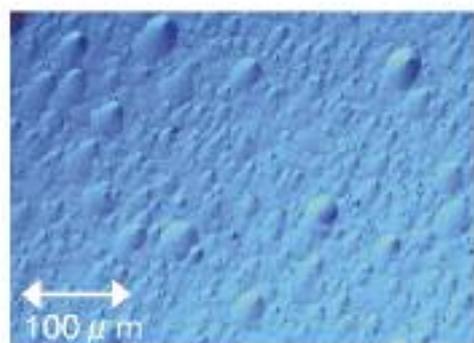


Fig. 4 Typical surface morphology of nitrogen doped diamond film grown on Ib substrate by differential interference microscope

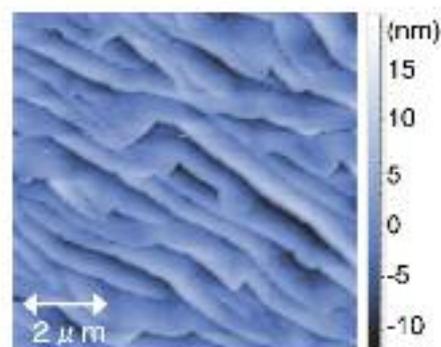


Fig. 5 Typical AFM image of nitrogen doped diamond film grown on Ib substrate.

Fig. 6 shows the Raman spectrum of the nitrogen-doped homoepitaxial diamond films on Ib substrates with the spectrum from a Ib substrate as a reference. The strong and sharp 1332cm⁻¹ peak characteristic of crystalline diamond is evident with only weak peaks due to non-diamond carbon components detected for the nitrogen-doped homoepitaxial diamond films. This result indicates that the bulk of obtained films are diamond with only a small concentration of non-diamond carbon.

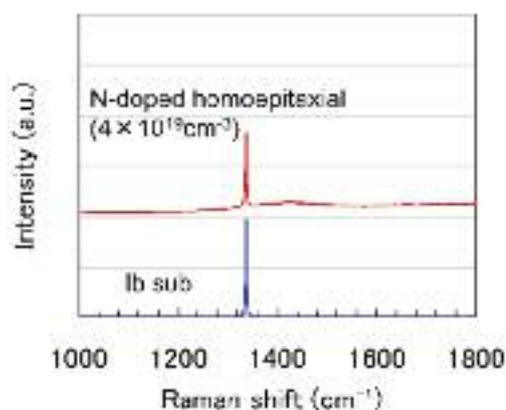


Fig. 6 Raman spectrum of nitrogen-doped homoepitaxial diamond films grown on Ib substrate and Ib substrate

Fig. 7 shows the typical thermionic electron emission characteristic obtained for the nitrogen doped homoepitaxial diamond film with nitrogen concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$. At a temperature $< 600^\circ\text{C}$ an emission current was detected which increased exponentially with temperature and achieving an emission current density of about 1.2 mA/cm^2 at 740°C . At temperature $> 740^\circ\text{C}$ the emission current started to decrease rapidly. This effect is attributed to evolution of the hydrogen passivation from the diamond surface, which in turn increases the electron affinity from a negative to a positive value¹³⁾.

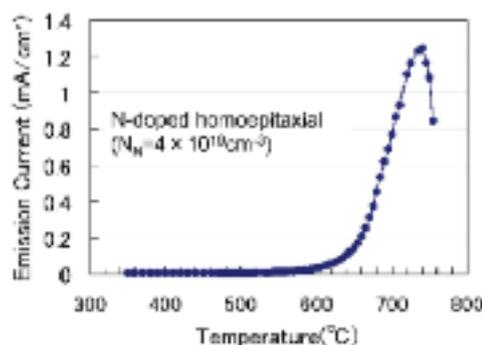


Fig. 7 Thermionic electron emission characteristic obtained for the nitrogen doped homoepitaxial diamond film with nitrogen concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$.

PEEM and T-FEEM images of hydrogen-terminated nitrogen doped homoepitaxial diamond film with nitrogen concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$ are shown in Fig. 8. The PEEM image shows a surface morphology similar to that observed by AFM, where brighter spots apparently correspond to non-epitaxial crystallites. With the UV lamp turned off T-FEEM images were obtained due to the thermal emission, and the imaging was achieved with the same applied field. T-FEEM could not be detected from the sample at temperatures below 250°C. However, at temperature > 350°C, the T-FEEM images were observed, and the intensity increased as the temperature increased. The T-FEEM image at 450°C clearly indicates that electron emission does not originate from localized surface regions such as non-epitaxial crystallites, but is uniformly distributed over the whole surface area. Thus field emission does not contribute significantly to the T-FEEM image.

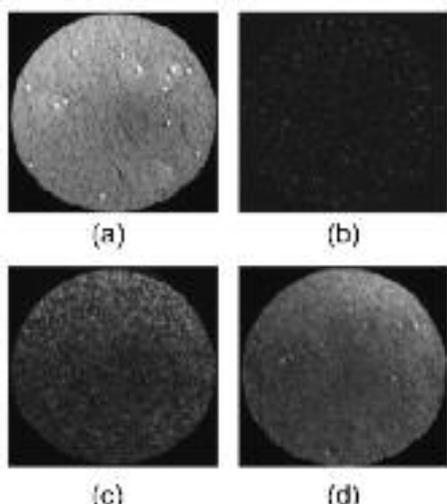


Fig. 8 PEEM and T-FEEM images(95 μm -field of view) of hydrogen-terminated nitrogen doped homoepitaxial diamond film with nitrogen concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$: (a) PEEM obtained with Hg arc lamp excitation; (b) T-FEEM at 250°C and (c) at 350°C (d) at 400°C (e) at 450°C

UPS and TES measurements were obtained to determine the relationship of the thermionic electron emission and the surface electronic properties for nitrogen doped homoepitaxial diamond film. Fig. 9 shows the UPS spectra of nitrogen-doped homoepitaxial diamond film with hydrogen termination at room temperature and 450°C. Since electrons are emitted from the conduction band, the effective work function of an NEA emitter is the energy difference between the Fermi level and the conduction band minimum at the surface. At room temperature, UPS indicates an effective

work function of 1.8eV. As the temperature is increased, the low energy cut off in the UPS increased and indicates a work function of 2.2eV at 450°C. However the shape of the low energy cut off of the photoemission spectrum is not sharp and there is also a possibility that the low energy cut off is influenced by charging of the sample.

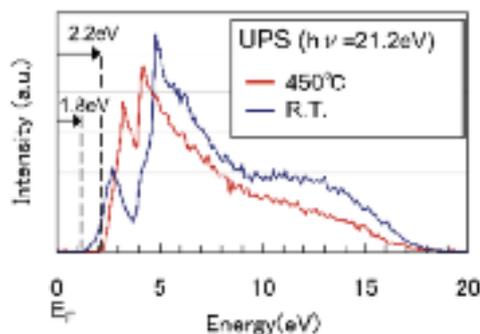


Fig. 9 UPS spectra of nitrogen-doped homoepitaxial diamond film with hydrogen termination at room temperature and 450°C. Blue and red line indicates spectra obtained at room temperature and 450°C, respectively.

Therefore, we performed TES measurement to determine the origin of the thermionic emitted electrons in the nitrogen-doped films more precisely. Fig. 10 shows the temperature dependent TES spectra of a nitrogen doped homoepitaxial diamond film with hydrogen termination. The thermionic emission spectra were observed at temperatures starting at 550°C with a low energy cut off at 2.4eV, corresponding to an effective work function of approximately 2.4eV. The intensity increased significantly with increased temperature consistent with the exponential increase observed in the I-T measurements. This result is also in agreement with the work function that was deduced from the UPS, which suggests that the thermionic electron emission originates from the conduction band of diamond.

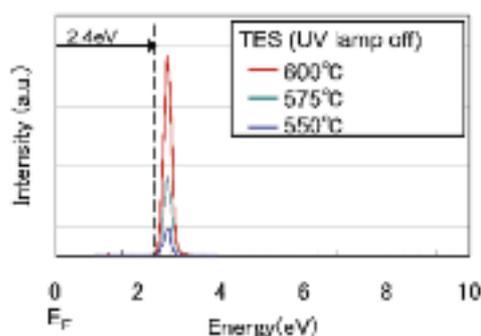


Fig. 10 TES spectra of nitrogen doped homoepitaxial diamond film with hydrogen termination. Blue, green and red line indicates spectra obtained at 550°C, 575°C and 600°C, respectively.

Fig. 11 shows the temperature dependent work function of nitrogen-doped homoepitaxial diamond film with nitrogen concentration of $\sim 4 \times 10^{19} \text{cm}^{-3}$ and Ib substrate with expected nitrogen concentration of $10^{19} \sim 10^{20} \text{cm}^{-3}$. The work function of the Ib substrate that was deduced from the TES is 2.2eV at 450°C, which is smaller than the 3.3eV result reported in previous studies ⁷⁾. The band diagram derived from the UPS is shown in Fig. 12. Noting that the Fermi level is 2.4eV at the surface and 1.7eV in the bulk, upward band bending of 0.7eV is estimated for this nitrogen-doped diamond. This value indicates reduced band bending and establishes the potential for electron emission devices based on nitrogen-doped diamond. The difference of the work function between the current and previous study is approximately 1.0eV ⁷⁾. The previous study employed a polished high temperature high pressure (HTHP) synthetic substrate, which may have significant variations in doping concentration and the polishing and surface treatment, may also contribute to the difference. It seems likely that the homoepitaxial sample would have more uniform doping with a greater nitrogen concentration, and the effect of polishing induced damage surface would also be minimized. We suggest that the additional electron concentration near the surface could partially fill the empty surface states that lead to the band bending.

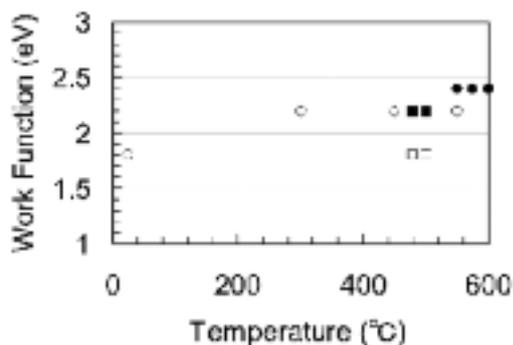


Fig. 11 Temperature dependence of work function of nitrogen-doped homoepitaxial diamond film and Ib substrate. Solid circles indicate work function of nitrogen-doped homoepitaxial film derived from TES. Open circles indicate work function of nitrogen-doped homoepitaxial film derived from UPS. Solid squares indicate work function of Ib substrate derived from TES. Open squares indicate work function of Ib substrate derived from UPS.

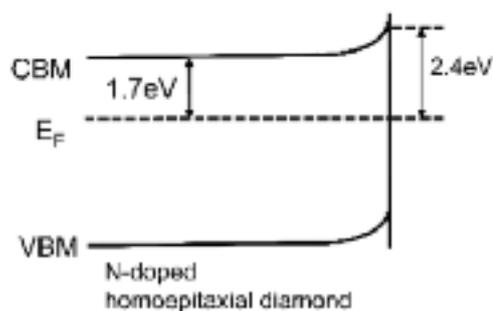


Fig. 12 Band diagram of nitrogen-doped diamond. CBM is the conduction band minimum; E_F , the Fermi level; VBM, the valence band maximum.

4. Conclusions

We have prepared nitrogen-doped homoepitaxial diamond films by plasma assisted chemical vapor deposition. Thermionic electron emission measurements in an UHV environment were conducted where the emission current was recorded as a function of emitter temperature. At a temperature $< 600^\circ\text{C}$ an emission current was detected which increased with temperature, and the emission current density was about 1.2mA/cm^2 at 740°C . PEEM and T-FEEM investigation of the NEA nitrogen-doped homoepitaxial diamond films showed uniform emission at 450°C . Thermionic emission and ultraviolet photoemission spectroscopy were employed to determine the temperature dependent electron emission energy distribution from the nitrogen doped homoepitaxial diamond films. The photoemission spectra indicated an effective work function of 2.4eV at 550°C . These values indicate reduced band bending and establish the potential for efficient electron emission devices based on nitrogen-doped diamond.

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