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Thermionic electron emission from nitrogen-doped homoepitaxial diamond

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ABSTRACT

Nitrogen-doped homoepitaxial diamond films were synthesized for application as low-temperature thermionic electron emitters. Thermionic electron emission measurements were conducted where the emission current was recorded as a function of emitter temperature. At a temperature <600 °C an emission current was detected which increased with temperature, and the emission current density was about 1.2 mA/cm² 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 2.4 eV at 550 °C. These values indicate reduced band bending and establish the potential for

efficient electron emission devices based on nitrogen-doped homoepitaxial diamond.

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1. Introduction

Thermionic electron emitters are a key component of high frequency vacuum devices and thermionic energy conversion devices. For both applications, there is a significant advantage to obtaining uniform thermionic emission at relatively low temperatures (<600 °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 donors [1–3]. In previous studies from our laboratory, 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 1.5-1.9 eV and an increased performance of thermionic electron emission [4,5]. 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 ~ 1.7 eV which would increase the work function of the material and raise the emission barrier [6]. In this

* Corresponding author. E-mail address: MITSUHIRO_KATAOKA@denso.co.jp (M. Kataoka). 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.

2. Experimental

Nitrogen-doped homoepitaxial diamond films were synthesized by plasma assisted chemical vapor deposition. Substrates used were $3 \times 3 \text{ mm}^2$ commercially available high-temperature high-pressure (HTHP) type-lb 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 50 Torr, 800 °C, and 1300 W, respectively. The incorporation of nitrogen in the films was evaluated by secondary-ion mass spectroscopy (SIMS) and it was $\sim 4 \times 10^{19} \text{ cm}^{-3}$. 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 532 nm excitation.

Thermionic electron emission measurements were conducted in a UHV environment with a base pressure $<5 \times 10^{-10}$ Torr, and the emission current was recorded as a function of emitter temperature. The apparatus included an anode movable 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.

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Table 1

Growth conditions for nitrogen-doped homoepitaxial diamond.

Source gases	H ₂ , CH ₄ , N
CH_4/H_2	0.05%
N / C	20
Pressure	50 Torr
Substrate temperature	~800 °C
MW plasma power	1300 W
Substrate	Ib, (001)

Photoelectron emission microscopy (PEEM) and thermionic fieldemission electron microscopy (T-FEEM) 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 5×10^{-10} Torr. Ultraviolet photoelectron spectra were obtained with He I (21.2 eV) radiation, and the spectrum of the emitted electrons was measured with a VSW-HA50 hemispherical analyzer operating at a resolution of 0.1 eV. 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. 1 shows a typical surface morphology of nitrogen-doped diamond films grown on an lb substrate. Non-epitaxial crystallites and pyramidal hillocks, which are often observed on (001) homoepitaxial CVD diamond, were detected [7–9]. Fig. 2 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 [10,11].

Fig. 3 shows the Raman spectrum of the nitrogen-doped homoepitaxial diamond films on lb substrates with the spectrum from the lb substrate as a reference. The strong and sharp 1332 cm⁻¹ peak characteristic of crystalline diamond is evident with only weak peaks due to non-diamond carbon components detected for the nitrogendoped homoepitaxial diamond films. This result indicates that the bulk of obtained films are diamonds with only a small concentration of non-diamond carbon.

Fig. 4 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 °C an emission current was detected which increased expo-



Fig. 1. Typical surface morphology of nitrogen-doped diamond film grown on lb substrate by differential interference microscope.



Fig. 2. Typical AFM image of nitrogen-doped diamond film grown on Ib substrate.



Fig. 3. Raman spectra of nitrogen-doped homoepitaxial diamond films grown on lb substrates and lb substrate.

nentially with temperature and achieving an emission current density of about 1.2 mA/cm² at 740 °C. At temperature > 740 °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 value [12].

PEEM and T-FEEM images of hydrogen-terminated nitrogendoped homoepitaxial diamond film with nitrogen concentration of \sim 4 × 10¹⁹ cm⁻³ are shown in Fig. 5. 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,



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



Fig. 5. PEEM and T-FEEM images (95 μ m-field of view) of hydrogen-terminated nitrogen-doped homoepitaxial diamond film with nitrogen concentration of ~4×10¹⁹ cm⁻³: (a) PEEM obtained with Hg arc lamp excitation; (b)T-FEEM at 250 °C;(c) at 350 °C and (d) at 450 °C.

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.

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. 6 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 1.8 eV. As the temperature is increased, the low energy cut off in the UPS increased and indicates a work function of 2.2 eV at 450 °C. However the shape of the low energy cut off of the



Fig. 6. UPS spectra of nitrogen-doped homoepitaxial diamond film with hydrogen termination at room temperature and 450 °C. Blue and red lines indicate spectra obtained at room temperature and 450 °C, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. TES spectra of nitrogen-doped homoepitaxial diamond film with hydrogen termination. Blue, green and red lines indicate spectra obtained at 550 °C, 575 °C and 600 °C, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

photoemission spectrum is not sharp and there is also a possibility that the low energy cut off is influenced by charging of the sample.

Therefore, we performed TES measurement to determine the origin of the thermionic emitted electrons in the nitrogen-doped films more precisely. Fig. 7 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 2.4 eV, corresponding to an effective work function of approximately 2.4 eV. 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



Fig. 8. Temperature dependence of work function of nitrogen-doped homoepitaxial diamond film and lb 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 lb substrate derived from TES. Open squares indicate work function of lb substrate derived from UPS.



Fig. 9. Band diagram of nitrogen-doped homoepitaxial diamond film. CBM is the conduction band minimum; $E_{\rm F}$ the Fermi level; and VBM, the valence band maximum.

function that was deduced from the UPS, which suggests that the thermionic electron emission originates from the conduction band of diamond.

Fig. 8 shows the temperature dependent work function of nitrogen-doped homoepitaxial diamond film with nitrogen concentration of -4×10^{19} cm⁻³ and lb substrate with expected nitrogen concentration of 10^{19} – 10^{20} cm⁻³. The work function of the lb substrate that was deduced from the TES is 2.2 eV at 450 °C, which is smaller with the 3.3 eV result reported in previous studies [6]. The band diagram derived from the UPS is shown in Fig. 9. Noting that the Fermi level is 2.4 eV at the surface and 1.7 eV in the bulk, upward band bending of 0.7 eV 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 1.0 eV [6]. 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 banding.

4. Conclusions

We have prepared nitrogen-doped homoepitaxial diamond films by plasma assisted chemical vapor deposition. Thermionic electron emission measurements in the UHV environment were conducted where the emission current was recorded as a function of emitter temperature. At a temperature <600 °C an emission current was detected which increased with temperature, and the emission current density was about 1.2 mA/cm² at 740 °C. PEEM and T-FEEM investigations 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 2.4 eV 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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