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Enhanced low-temperature thermionic field emission from surface-treated N-doped diamond films

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Abstract

Nitrogen-doped diamond films have been synthesized for application as a low-temperature thermionic field-emission cathode. The critical result of this study is the observation of uniform electron emission from UV photo-excitation and from thermionic field emission for films terminated with hydrogen or a 0.3-nm Ti layer. The samples were imaged with photoelectron emission microscopy (PEEM) and thermionic field-emission electron microscopy (T-FEEM) at temperatures up to 900 °C, and the electron emission current was recorded vs. the applied voltage. Hydrogen-passivated films show enhanced electron emission, but become unstable at elevated temperatures, while Ti-terminated films showed similar enhanced emission at temperatures up to 950 °C. Temperature-dependent I/V measurements show strongly increased electron emission at higher temperatures, suggesting that electron emission originates from the conduction band. These results indicate a promising new material for the production of low-temperature, high-brightness electron sources. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemical vapor deposition (CVD); Diamond; Field emission

1. Introduction

Carbon based-electron sources are of great interest due to their low threshold fields. Extensive studies have led to considerable progress in lowering the threshold field to as low as 0.5 V μm^{-1} [1]. Emission from these films is not uniform, but appears to originate from strongly localized emission sites, thus making them not well suited for large-area electron emitters. In this paper, we report on uniform electron emission from carbon-based films as a function of temperature with different surface treatments to obtain a negative electron affinity (NEA) of the diamond film. It is well known that the (100), (110) and (111) surfaces of diamond exhibit a negative electron affinity (NEA) when terminated with hydrogen [2,3]. In the case of a NEA surface, the vacuum level is pulled below the conduction band minimum (CBM) at the surface, allowing electrons to be released into vacuum without an energy barrier at the surface. Whether a surface exhibits NEA or not can be determined by employing photo-excitation of the electrons into the conduction band minimum and observing electron emission from the surface [4,5].

Electron emission microscopy can be used to image the electron emission properties of a surface in a controlled UHV environment. Our instrument, an Elmitec© electron emission microscope, can be operated in different modes in order to investigate electron emission originating from various sources. Illuminating a sample with UV light from a Hg arc lamp and observing electron emission is termed photoelectron emission microscopy (PEEM). Without light irradiating the sample, electron emission is due to the applied field, and we have termed this mode field-emission electron microscopy (FEEM). The apparatus is equipped with a sample stage that allows sample temperatures of up to 1200 °C and real-time imaging of thermionic electron and field emission. We have termed this imaging condition as thermionic-field electron emission microscopy (T-FEEM). In addition, the electron emission current can be recorded for any operating mode mentioned above [6].

We have investigated the electron emission properties of nitrogen-doped diamond films that have been surface-treated in both PEEM and FEEM modes as a function of sample temperature up to 950 °C. To date, n-type

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doping of diamond is difficult to obtain. The most common approach is to employ nitrogen doping, which exhibits a conductivity activation energy of 1.7 eV for substitutional nitrogen, suggesting that the energy level caused by the substitutional nitrogen lies 1.7 eV below the CBM [7].

Several groups have investigated hydrogen termination and electron emission properties of CVD diamond [8,9]. It is well established that a hydrogen passivation layer on a diamond surface enhances photoemission due to lowering of the electron affinity χ, to such an extent that χ becomes negative and the vacuum level drops below the conduction band edge [10]. For nitrogen-doped diamond, the (100)-(2×1):H surface is expected to exhibit strong upward band-bending at the surface [11]. This effect could induce a surface barrier, preventing CBM electrons from being released into vacuum. So far, hydrogen has been the most commonly used material for inducing NEA on diamond surfaces to enhance electron emission. In prior studies by our group, it was established that a Ti layer could also induce NEA on diamond surfaces [12]. In this study, we have investigated the effect of a thin metal layer of titanium on the electron emission properties at elevated temperatures for highly nitrogen-doped diamond films. We find that titanium shows superior properties in enhancing electron emission at higher temperatures compared to hydrogen.

2. Experimental details

The substrate material used for this study was Si⟨100⟩, with a diameter of 25 mm and a resistivity of 1 Ω?cm, and 9×9-mm^2 SiC squares. The first step included a 30-min ultrasonic abrasion in a diamond/titanium/ethanol suspension, followed by a rinse with methanol and drying with nitrogen gas. Using a diamond/metal powder-based suspension results in an enhanced nucleation density compared to a diamond-only suspension [13]. The CVD reactor used is a 1500-W ASTeX IPX3750 microwave-assisted CVD system with an RF induction-heated graphite susceptor. The process gases were zero-grade N_2, H_2 and CH_4. During film growth, laser reflectance interferometry (LRI) was used to in situ monitor the thickness of the diamond layer.

The growth of the N-doped diamond films was divided into three steps: (1) establishment of the nucleation layer; (2) growth of the N-doped film; and (3) post-surface treatment. The conditions for the nucleation layer were: 400 sccm H_2; 8 sccm CH_4; chamber pressure, 20 torr; substrate temperature, 740 °C; and microwave power, 600 W. After formation of the nucleation layer, the conditions were changed to: 437 sccm H_2; 2.5 sccm CH_4; 60 sccm N_2; pressure, 50 torr; substrate temperature, 890 °C; and microwave power, 1300 W for a nitrogen-doped diamond film with $N/C=48$. By growing for approximately 20 h, films with a thickness of approximately 2.5 μm were fabricated. Shutting off the gas flows and turning off the heater to cool down the sample terminated the growth. The high hydrogen concentration in the plasma ensured that the diamond surface became hydrogen-terminated, which resulted in a clean surface for subsequent processing. For some samples, the diamond film was then transferred into an electron-beam metallization chamber to deposit a titanium layer with a thickness of approximately 3 Å. The metal deposition was performed at room temperature.

PEEM and FEEM measurements were carried out in an Elmitec UHV photoelectron emission microscope. Measurements were obtained at a base pressure of $< 1\times10^{-10}$ torr. The field of view can be changed from 150 to 1.5 μm, with a resolution better than 15 nm. For all measurements, a high voltage of 20 kV was applied between the anode and the sample surface, and the anode was at a distance of 2–4 mm from the surface (resulting in an applied field of 10–5 V μm^{-1}). In the PEEM measurements, a mercury arc lamp was used as the UV light source. In the FEEM measurements, no UV excitation was employed, and emission was due to the high applied field. To compare the morphology of the samples with images obtained by PEEM and T-FEEM, atomic force microscopy (AFM) measurements were performed.

The Elmitec UHV photoelectron emission microscopy system has sample heating up to 1200 °C to obtain T-FEEM images. The electron emission current from the sample surface can be monitored and recorded to obtain current–voltage dependence. Electrons emitted from the sample pass through a perforated anode and are imaged using electron optics. The electrons emitted are intensified with a microchannel plate and imaged with a fluorescent screen. A CCD camera is used for image capturing. The images reported here have been digitally processed to remove imperfections of the image intensifier.

3. Results and discussion

The influence of nitrogen on the growth and properties of diamond films has been described in several publications [14,15]. Increasing the nitrogen content in the growth chamber is followed by a change in the Raman spectrum. Nitrogen causes an increase in the sp^2 bonding signatures and a broadening of the full width at half-maximum (FWHM) of the 1332-cm^{-1} diamond peak. Displayed in Fig. 1, the Raman spectrum of a 0.5-μm diamond film shows a broad spectral background extending from 1100 to 1600 cm^{-1}. The spectral components attributed to sp^2-bonded carbon include the 1355–1580-cm^{-1} doublet due to microcrystalline graphite, and the broad peak centered near 1500

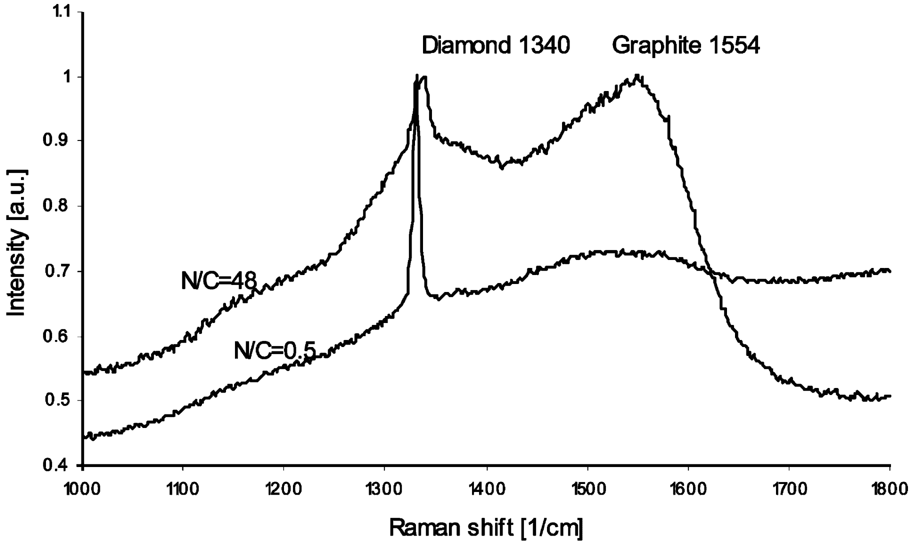

Fig. 1. Raman spectra of nitrogen-doped diamond films with N/C = 48 and N/C = 0.5, showing a broadened diamond peak and spectral components attributed to sp^2 bonding, particularly for the diamond film with higher nitrogen concentration.

cm^{-1} attributed to sp^2 bonding in or around diamond crystals. [16] A feature at ~1140 cm^{-1} has been attributed to disordered sp^3-bonded carbon, and the broadening and shifting of the 1332-cm^{-1} diamond peak indicates small grain size, strain and/or the presence of defects or impurities [17]. It should be noted that Raman spectroscopy is approximately 75-fold more sensitive to sp^2-bonded carbon sites than it is to crystalline diamond when 514.5-nm excitation is used [18]. It is evident that the film has a significant diamond crystal component, but it also exhibits sp^2-bonded carbon, with the variations in bonding on a nanometer scale. When using nitrogen gas as the nitrogen dopant source, it was found that the nitrogen concentration in the diamond film is low [19].

A PEEM image of a hydrogen-terminated N-doped diamond film at room temperature is shown in Fig. 2. The image indicates that photoelectron emission does not originate from localized surface regions, but is uniformly distributed over the whole surface area. AFM measurements of the surface reveal a similar, fine-textured, grainy structure of an overall smooth film with a few elevated points. This surface topography is also imaged by PEEM, where brighter spots correspond to raised features with a higher local electric field. The images resulting from the PEEM measurements can be understood in terms of photoelectron emission from NEA diamond [3]. The photo-excited electrons in the conduction band of diamond are emitted into vacuum following the theory of photoemission. Note that the emission is uniform over the surface, with no evidence of localized emission often observed for field emission from carbon-based cold cathode materials.

With the UV lamp turned off, FEEM images were obtained due to the applied field. For the H-terminated N-doped diamond, FEEM could not be detected from

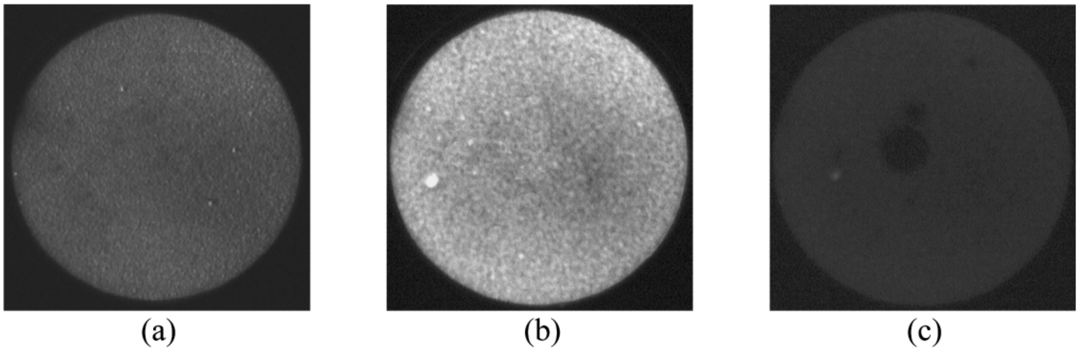

Fig. 2. Electron emission microscope images (50-μm field of view) of H-terminated N-doped diamond: (a) PEEM obtained at room temperature with Hg arc lamp excitation; (b) T-FEEM image at 725 °C at $t = 0$ min; and (c) after 10 min. The evident decrease in intensity is attributed to the degradation of the hydrogen passivation that induces the NEA.

the sample at room temperature. These results are consistent with our prior studies, which showed a high threshold for room-temperature field emission from most N-doped diamond films [20]. However, at elevated temperature, the T-FEEM (thermionic FEEM) images were observed with an intensity similar to that of the PEEM.

The stability of the hydrogen passivation layer at elevated temperatures shows rapid degradation. Fig. 2 shows T-FEEM images of the $N/C=48$ nitrogen-doped diamond film when the temperature has reached 725 °C. After 10 min, a subsequent T-FEEM image indicates that the thermionic electron emission has significantly decreased. Current–voltage measurements, as shown in Fig. 3, also indicate a drop in the electron emission current at elevated temperatures. We suggest that the change is due to evolution of the hydrogen passivation from the diamond surface, which in turn increases the electron affinity from a negative to a positive value [8].

Similar T-FEEM measurements were obtained from the Ti terminated nitrogen-doped diamond film (grown on SiC). Fig. 4a,b show T-FEEM images with a 150-μm field of view and substrate temperatures of 750 and 950 °C, respectively. The higher temperatures were not possible for H-terminated diamond surfaces. From the T-FEEM images, a very uniform electron emission can be observed that increases in intensity with increasing temperature. It is evident that the FEEM is very temperature-dependent, with a strong increase above 700 °C. The uniformity of the emission suggests that the electrons may originate from the conduction band of diamond, or alternatively, from defect states in the bandgap. If this were the case, then the uniformity of the emission would require that the defects be uniformly distributed throughout the film. Besides the single substitutional donor level at 1.6 eV below the CBM, nitrogen-doped diamond has been found to incorporate other defect levels [21], and the π-bonded sp^2 regions will also introduce states in the gap [8]. These defect states may play an important role in enhancing electron emission, especially at high fields.

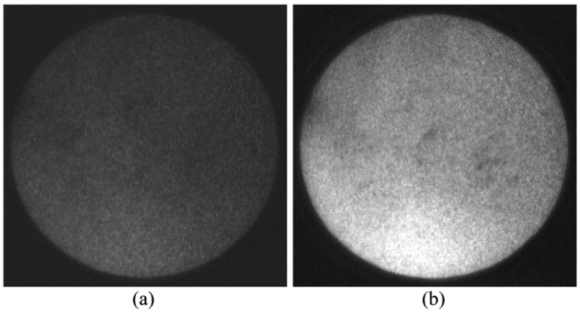

Fig. 4. T-FEEM images (150-μm field of view) of Ti-terminated N-doped diamond at (a) 750 and (b) 950 °.

For each sample temperature of 700, 750, 800, 850, 900 and 950 °C, an I/V curve was recorded. Fig. 5 shows a set of I/V curves obtained at various temperatures. At low fields, we find a nearly constant value of the electron emission current. Increasing the anode voltage beyond 15 kV results in exponential behavior, which dominates the emission current characteristics. We have calculated the activation energy from the Arrhenius plot of the emission current at low voltage of <10 kV to be ~ 1 eV, suggesting a contribution to the emission current from nitrogen donor levels and defect states. Electrical conductivity measurements on type IIa natural diamond, which has nitrogen as the dominant impurity, shows an exponential temperature dependence of the carrier density, and approximately two orders of

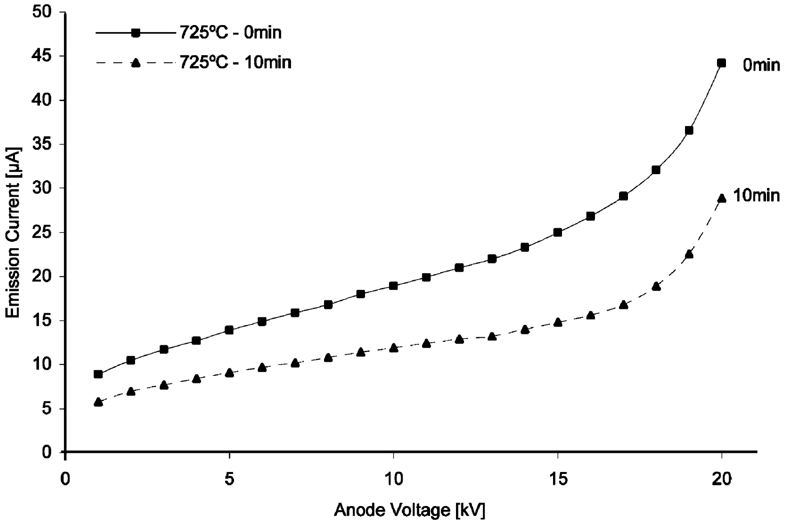

Fig. 3. I/V measurements of a hydrogen-passivated, nitrogen-doped diamond film after reaching 725 °C, at $t=0$ min and after 10 min, showing the reduction in the electron emission current.

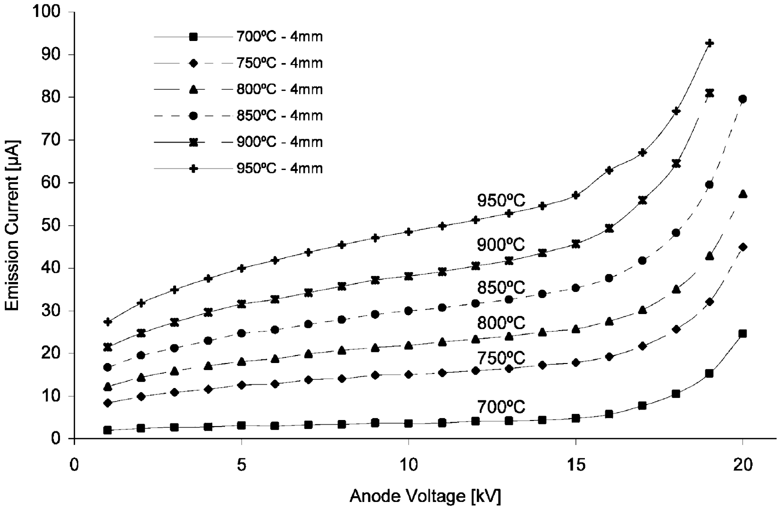

Fig. 5. The emission current vs. applied voltage obtained in the electron emission microscope for a Ti-terminated N-doped diamond film. Note that the baseline signal increases with temperature. The distance between sample and anode was 4 mm.

magnitude of change that is attributed to changes in the mobility. For type IIa natural diamond, Han et al. reported an activation energy of 1.4 eV, which likely reflects the excitation of electrons from nitrogen levels [22].

The emission characteristics presented here suggest a thermionic contribution to the electron emission of N-doped diamond films at elevated temperatures. It appears that the emission at low fields could be attributed to thermionic emission of electrons in the conduction band of diamond. The exponential increase in the current at higher fields indicates a tunneling process or thermionic emission over a potential barrier. Band bending at the back or front surface or hopping conduction could contribute to this effect. The details of the emission process in N-doped diamond require further study to determine the origin.

4. Conclusions

We have prepared nitrogen-doped diamond films by plasma-assisted CVD. Raman spectroscopy showed a broadened diamond peak and the presence of sp^2 bonding in the film. NEA surfaces were obtained with H and Ti termination. PEEM investigation of the NEA nitrogen-doped diamond films showed uniform electron emission at room temperature. At temperatures below 500 °C, FEEM does not resolve electron emission from the specimen. Increasing the sample temperature up to 720 °C revealed a strong increase in the electron emission, suggesting that electrons from the nitrogen donor levels are excited into the CB. It was also noted that defects and band bending could play a role in the emission process. The extent to which this affects emission properties has to be explored in further studies. T-FEEM measurements at elevated temperatures showed the importance of a stable surface passivation that induces a NEA surface. It has been shown that a hydrogen passivation layer significantly degrades at temperatures of approximately 725 °C. In contrast, a titanium-passivated surface allows stable electron emission up to 950 °C.

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