Imaging electron emission from diamond film surfaces: N-doped diamond vs. nanostructured diamond

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Abstract

This study reports direct imaging of electron emission from two different classes of diamond containing films that were prepared by microwave plasma chemical vapor deposition. These are N-doped, and nanostructured diamond containing films. The electron emission is excited by UV light (photoemission) or by an applied field (field emission). The photo electron emission microscopy (PEEM) of the N-doped films exhibited uniform emission, and upon heating to ∼ 700°C, field electron emission microscopy (FEEM) of the films showed similar uniform emission. In contrast, FEEM of the nanostructured films showed high brightness, localized emission sites at room temperature. The results indicate different processes for electron emission from nanostructured and N-doped diamond films. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

There have now been many reports of electron emission from carbon films at applied fields of less than 10 V/μm. Most of these films exhibit high sp^2 content and/or are characterized as nanostructured [1]. In contrast, there are conflicting results on the emission properties of N-doped diamond films. We have recently shown that N-doped, MPCVD diamond with a low concentration of sp^2 bonding, exhibits emission only with a very high applied field (> 100 V/μm) [2]. In addition, these films are prone to arc damage events.

The observation that hydrogen terminated diamond surfaces exhibit a negative electron affinity (NEA) has led researchers to explore whether electron emission could be obtained at very low applied fields [3,4]. Field emission measurements from B-doped, p-type, single crystalline diamond surfaces have displayed moderate field emission thresholds (> 20 V/μm) [5]. One study of N-doped, n-type, single crystal diamond showed emission with a very low electric field at the surface (< 1 V/μm) [5]. However, a high applied voltage was necessary, and it was suggested that most of the voltage was dropped across the back contact that supplies electrons to the highly resistive diamond [5]. Emission of conduction band electrons from NEA surfaces would be expected to be relatively uniform since field enhancement would not be required [6].

This report addresses the spatial variation of the field emission from these different types of films. Previous studies of diamond containing films with low field emission thresholds have established that the emission originates from highly localized sites [7]. These measurements are typically obtained with a phosphor anode rather than direct imaging [8]. Emitting site densities of 10^2 to 10^6 cm^{-2} are often observed. Measurements of the electron energy distribution of these films suggest that the field emission is due to electrons near the Fermi level of the material, and the work function of the surface is found to be approximately 5 eV [9].

It is evident that imaging of electron emission from diamond containing films could provide significant in-

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sight into the emission mechanisms from these materials. The experiments presented here employ electron emission microscopy in which the emitted electrons are directly imaged with a resolution of less than 100 nm [10,11]. The measurements are obtained in two modes, photoemission and field emission. In photo-electron emission microscopy (PEEM), ultra violet light incident on the sample results in photoemission. The electrons are accelerated with a 20-kV potential, and electron optics image the emission. The accelerating voltage results in an applied field of up to 10 V/μm. Thus the applied field alone (with no UV light) can result in electron emission from some films, and the field emission can be directly imaged. This mode is termed field electron emission microscopy (FEEM).

In this study, we report PEEM and FEEM imaging of two types of diamond containing films. To explore the possibility of emission from a NEA surface, we have examined N-doped films. To explore the highly localized emission sites, nanostructured diamond was imaged with PEEM and FEEM. In all cases the sample surfaces were characterized with atomic force microscopy and the sp^2 and sp^3 bonding was compared with Raman spectroscopy.

2. Experimental

Diamond containing films were prepared in a microwave plasma enhanced chemical vapor deposition system. By varying the plasma conditions, the substrate temperature, and the gas phase concentrations and pressure, diamond containing films could be prepared with N-doping or as highly defective nanostructured diamond.

The growth of N-doped diamond films was divided into three steps: (1) deposition of the nucleation layer; (2) N-doped diamond film growth; and (3) surface post treatment. For the nucleation layer a thin, high sp^2 containing diamond film was grown on a pretreated silicon or molybdenum substrate. The growth conditions for the nucleation layer were 400 sccm H$_2$, 8 sccm CH$_4$, chamber pressure of 20 torr, substrate temperature of 780°C and a microwave power of 600 W. After deposition of the nucleation layer the flow rates of the process gases were changed to 437 sccm H$_2$, 2.5 sccm CH$_4$ and 60 sccm N$_2$. The growth temperature was increased to 910°C, the chamber pressure was increased to 50 torr, and the microwave power was increased to 1300 W. After the desired film growth thickness, the diamond film surface was then treated with H$_2$ plasma for 5 min at a pressure of 20 torr.

With increasing nitrogen content in the diamond film a decrease in the quality of the film can be observed. Raman scattering spectra show a broad graphitic peak and a broadened diamond peak. These features are attributed to the distortion in the crystal structure induced by the atomic nitrogen, since the C−N bond is approximately 36% longer than the C−C bond. The details of the Raman spectra of similarly prepared N-doped films have been reported previously [2].

Nanostructured diamond films were prepared in the same microwave plasma chemical vapor deposition system as the N-doped diamond films. These films were grown on pretreated silicon or molybdenum substrates under flows of 180 sccm H$_2$ and 20 sccm CH$_4$. The growth conditions were: chamber pressure of 20 torr, substrate temperature of 900°C, and microwave power of 900 W.

Raman spectroscopy indicates a high fraction of sp^2 bonding in these films with broad peaks at 1340 and 1580 cm^{-1}. In addition, a small shoulder at 1332 cm^{-1} has been detected in some of the samples indicating sp^3 bonded diamond in the films. The surfaces were also characterized with AFM. The RMS roughness of the film used in this study was measured to be 11 nm and the average roughness was 9 nm. The AFM measurements indicate a relatively smooth surface for these nanostructured films with many grains and grain boundaries.

The PEEM and FEEM measurements were completed in an Elmitec UHV-photo electron emission microscope [10]. Measurements were obtained at a base pressure less than 3×10^{-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 is applied between the anode and the sample surface, and the anode is a distance of 2 mm from the surface. 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 the emission was due to the high applied field.

The system has sample heating up to 1200°C, and FEEM or PEEM images can be obtained with the sample at elevated temperature. 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 image is intensified with a double microchannel plate and a fluorescent screen. A CCD camera is used for image capturing. The gain of the system is dependent on the voltage on the image intensifier. The images reported here have been digitally processed to remove dark regions of the intensifier.

3. Results

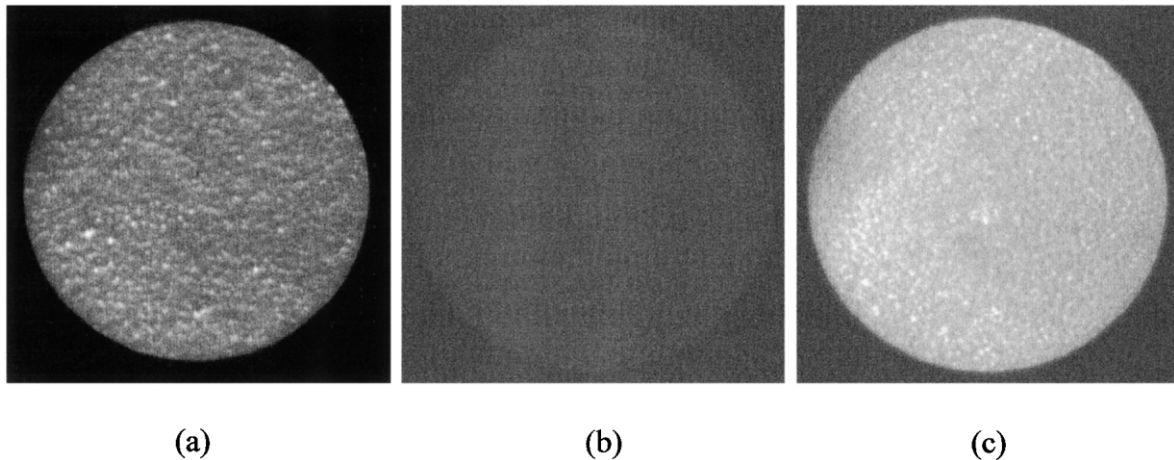After AFM and Raman characterization, the electron emission was imaged for an N-doped sample and a

Fig. 1. PEEM and FEEM of N-doped diamond film: (a) PEEM at room temperature; (b) FEEM at 640°C; (c) and FEEM 720°C. All images were obtained at a channel plate voltage of 1.55 kV, and the field of view is 20 μm.

nanostructured sample. The results presented here focus on two samples, but several samples of each type were examined and the results were essentially the same for all similar samples.

Our prior studies described field emission measurements from both samples type using a variable distance anode probe [2]. The measurements showed typical values of 4 V/μm for the nanostructured film and greater than 100 V/μm for the N-doped film measured at room temperature [2].

3.1. N-doped diamond film

Shown in Fig. 1a is the PEEM measurements of the N-doped film obtained at room temperature. The image displays uniform electron emission over the whole sample surface with a fine textured grainy structure that is comparable to SEM images of the same surface. Images resulting from PEEM measurements can be understood in terms of photoelectron emission from NEA diamond. The NEA of hydrogen terminated diamond allows electrons excited into the conduction band to escape into vacuum.

As noted in the previous section, the high applied field in the microscope can lead to FEEM images. By turning off the Hg-arc lamp and increasing the sample temperature, FEEM of the nitrogen doped diamond film can be observed. No image or emission could be detected below 400°C. The FEEM images were obtained at various temperatures but at a constant channel plate voltage. Fig. 1b,c shows FEEM images with a 20-μm field of view at a channel plate voltage of 1.55 kV. The images correspond to substrate temperatures of 640°C and 720°C, respectively. From the FEEM images in Fig. 1b,c a very uniform electron emission can be observed that increases in intensity with increasing temperature. Heating above 900°C results in a

significant decrease in emission attributed to the loss of hydrogen from the surface and an increase in the electron affinity.

For each sample temperature an I/V curve was recorded. At low fields we find a linear dependence of the electron emission current to the applied voltage. Increasing the anode voltage beyond 15 kV an exponential behavior dominates the emission current characteristics. Electrical conductivity measurements on type IIa natural diamond, that has nitrogen as the dominant impurity, show an exponential temperature dependence of the carrier density, and approximately two orders of magnitude of change of the conductivity that is attributed to changes in the mobility. For type IIa natural diamond Han et al. report an activation energy of 1.4 eV that likely reflects the excitation of electrons from nitrogen levels [12]. The emission characteristics at elevated temperatures indicate a thermionic contribution to the electron emission current.

3.2. Nanostructured diamond films

Nanostructured diamond films consist of many nanometer scale grains, and the films exhibit a high fraction of sp^2 bonding. The emission of these films, characterized by the electron emission microscope, can be divided into two distinct origins, emission sites and the background. Emission sites are small, autonomous, highly emitting sites that occur at a low density. The background of the sample is observed to emit only under the excitation of UV light. However, the emission displays the same uniformity as the PEEM of the N-doped samples.

Fig. 2a displays an AFM scan over a 5×5 μm region. It is evident that this film is rather smooth, yet the film shows field emission at applied fields of less

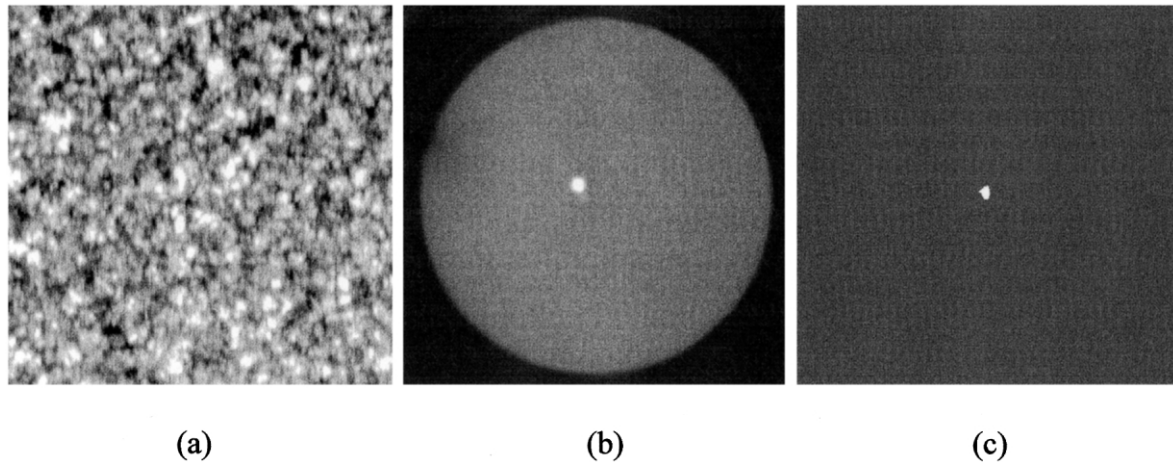(a)   (b)   (c)

Fig. 2. AFM, PEEM and FEEM of nanostructured diamond film: (a) AFM, 5 μm field of view, RMS roughness 11 nm, average roughness 9 nm; (b) PEEM at room temperature, channel plate 1.14 V; (c) FEEM at room temperature channel plate 1.452 V. The PEEM and FEEM images have a 150-μm field of view.

than 4 V/μm. Fig. 2c shows a FEEM image of the nanostructured diamond film in a region with an emission site. This picture was obtained at a 150-μm field of view, 1.452 V channel plate voltage, and room temperature. The strong emission of the site is evident while no emission from the background can be detected. FEEM images show identifiable emission sites which are separated by average distances of > 150 μm. The densities of these sites is on the order of 10^4 sites per cm^2. Fig. 2b shows a PEEM picture of the film at a 150-μm field of view, 1.14 V channel plate voltage, room temperature, and with a Hg arc lamp as the UV light source. In addition to the emission site, uniform emission from the background is now detectable (Fig. 2).

4. Discussion

The experimental results are summarized in the following. Highly localized strong emission sites are observed with nearly equal intensity in both FEEM and PEEM from nanostructured diamond. In regions where there is no localized emission, the surface exhibits uniform PEEM but FEEM is not detected. For the N-doped films, uniform PEEM is observed at all temperatures. At low temperatures, FEEM is not observed from these films, but at approximately 700°C uniform PEEM and FEEM are observed with nearly equal intensity.

While there have been many models to try to explain the electron emission from diamond containing films, two limiting cases represent many of the proposed processes. In one case it is proposed that the emission is due to field enhancement. Field enhancement means that the field is not uniform at the surface. This model naturally leads to a surface with non-uniform emission. Alternatively, if electrons are excited into the conduction band of NEA diamond, then the uniform density

of conduction band electrons should lead to uniform emission.

With these two limits in mind, we can now consider the results presented here. The nanostructured diamond emission may be attributed to field enhancement at the surface. This is also consistent with the electron energy distribution measurements that indicated emission from the Fermi level [9].

The uniform emission from the N-doped surfaces may then be considered to be emission from the NEA surface for electrons thermally excited into the diamond conduction band.

There are still significant questions to be addressed. In the nanostructured diamond surface, the samples exhibit a relatively smooth surface, and geometric field enhancement seems unlikely. It has been suggested that highly conductive grain boundaries in an insulating film could also lead to field enhancement due to the conducting filaments [13]. Given the high density of grains, and low density of emission sites, it is evident that the emission site must have some special character.

There are also questions related to the proposed conduction band emission from the N-doped diamond. While these films have a much lower sp^2 fraction than the nanostructured diamond, there is still significant sp^2 bonding in the films. These defects may provide states in the gap. It is possible that the emission originates from a nearly uniform distribution of defect states. Certainly electron energy distribution would be an important measurement, but it must be obtained with the sample at high temperatures.

5. Conclusions

In these studies, imaging of field emission and pho-

toemission from diamond film surfaces has been accomplished with a high-resolution photo-electron emission microscope (PEEM). Measurements obtained without UV light display field emission (FEEM) at applied fields of ~ 10 V/μm. N-doped diamond films have been produced by MPCVD. Field emission I/V measurements show very high threshold fields of > 100 V/μm. The surfaces display uniform photoemission in PEEM at all temperatures, but no FEEM images are detectable below 500°C. At ~ 680°C the FEEM and PEEM images are nearly identical in intensity and uniformity. In contrast, the nanostructured diamond films show field emission at applied fields of 4 V/μm. These films show high brightness, localized emission sites in FEEM images which are separated by average distances of > 150 μm. The results indicate that two different emission processes contribute to the observed field emission in the two types of samples. It is suggested that field enhancement plays a significant role in the emission from nanostructured diamond, while the presence of a NEA is required for the uniform emission observed for the N-doped films heated to ~ 700°C.

Acknowledgements

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