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Measurement of field emission from nitrogen-doped diamond films

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Abstract

This study explores issues related to the measurement of the field emission properties of nitrogen-doped diamond grown by microwave plasma chemical vapor deposition (CVD). Growth conditions have been optimized to produce films with a low concentration of sp^2-bonded carbon which results in high electrical resistance. Field emission characteristics were measured in an ultrahigh vacuum with a variable distance anode technique. For samples grown with gas phase [N]/[C] ratios less than 10, damage from micro-arcs occurred during the field emission measurements. Samples grown at higher [N]/[C] content could be measured prior to an arcing event. The occurrence of a micro-arc is related to the film properties. The measurements indicate relatively high threshold fields (> 100 V μm^{-1}) for electron emission.

Keywords: Field emission; Nitrogen-doped diamond; Microwave plasma chemical vapor deposition

1. Introduction

The observation of a negative electron affinity (NEA) for properly prepared diamond surfaces has led to the possibility of using diamond as a cold cathode material [1–5]. The ideal semiconductor cold cathode material would exhibit a NEA for n-type doped material. Nitrogen has a high solubility in diamond and is found in both natural and synthetic diamonds. In synthetic high pressure, high temperature (HPHT) type-Ib single crystal diamond, nitrogen is present in primarily single substitutional form with a relatively deep donor level located ~ 1.7 eV below the conduction band minimum [6,7].

In fact, in 1996 Geis et al. reported an enhancement of field emission properties of single crystal nitrogen-doped diamond [8]. More recently, Okano et al. [9] reported low field emission thresholds for nitrogen-doped chemical vapor deposition (CVD) diamond films. However, it has been shown that nitrogen incorporation leads to significant changes in the film morphology and in the relative amount of sp^2-bonded carbon [10].

In 1991, J. Mort et al. measured the electrical conductivity of undoped and nitrogen-doped films deposited by hot filament CVD [11]. In that study, electrical measurements of undoped diamond films indicated the conductivity was due to transport through in-gap defect states. Furthermore, it was established that these states were identified as acceptors. For nitrogen-doped films, it was observed that the electrical conductivity was less than that for undoped diamond films by a factor of 10^3 at room temperature and 10^6 at 400 K. This effect was attributed to the compensation of the defect acceptor states by nitrogen donors.

This study explores the field emission properties of high quality, nitrogen-doped diamond films grown by microwave plasma CVD. The high quality films employed here exhibit low sp^2 concentrations as indicated by Raman analysis and their high electrical resistance. In contrast to the reports described above, this study

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indicates that nitrogen doping of high quality diamond films results in field emission thresholds with average fields often exceeding 100 V μm^{-1}. In addition, arcing is frequently observed during field emission characterization causing extensive physical damage to the sample.

2. Experimental

Nitrogen-doped diamond films were deposited in a commercially available ASTeX HPMS stainless steel microwave (2.45 GHz) plasma CVD deposition chamber. The conventional gas mixtures of hydrogen and methane were used as the growth precursors. Nitrogen could be added as an impurity to the process gas with gas phase atomic nitrogen to carbon ratios ([N]/[C]) from 0 to 80. The film growth and characterization are described in more detail elsewhere [12].

Polycrystalline diamond films containing nitrogen were deposited on 25-mm diameter n-type (1 $\Omega \cdot$cm) Si(100) substrates or on polycrystalline Mo substrates. Nucleation was enhanced through diamond grit polishing, and nucleation densities of 10^9 cm^{-2} or greater was achieved. This is critical for the formation of continuous films used in this study.

Diamond nucleation was achieved at $\sim$760°C surface temperature, 600 W microwave power, 20 torr chamber pressure, and at a flow rate of 400 sccm using process gases consisting of 2 vol.% methane in hydrogen. Following the nucleation step, the substrate temperature, microwave power, chamber pressure, and process gases were changed to the growth conditions. Nitrogen-doped diamond films were grown at substrate temperatures from 800 to 900°C, 1300 W microwave power, and 50 torr chamber pressure. The growth process gases consisted of 0.5 vol.% methane and 0–12 vol.% nitrogen in hydrogen at a total flow rate of 500 sccm.

Prior to field emission measurements, the diamond samples were typically exposed to a remote hydrogen plasma to remove adsorbed species and hydrogen terminate the surface. The hydrogen plasma clean consisted of a 1-min exposure to a 50-W r.f. plasma discharge at $\sim$25 mtorr. The sample temperature was 500°C during the plasma treatment. This atomic hydrogen exposure has been shown to induce a NEA on several different diamond surface orientations [3].

The field emission measurements employed a variable distance anode, which was stepped toward the surface and current–voltage (I–V) measurements were obtained at various anode-to-sample distances. The measurements were conducted in a UHV environment with pressures typically $< 5 \times 10^{-9}$ torr. A cylinder of molybdenum (3 mm or 1 mm in diameter) was chosen as the anode for these measurements. The end of the cylinder was either polished flat or polished to a very high radius of curvature (typically > 5 mm) to minimize edge effects. The I–V measurements are acquired with a computer controlled Keithley 237 source-measure unit (SMU). Although the anodes used in this study were rounded, it is assumed that the electric field between the anode and the sample surface can be modeled by the parallel plate geometry. This assumption is valid since the radius of curvature is very large in comparison to the distance, d, between the anode and the sample (cathode). In the parallel plate geometry the electric field is given by $E = V/d$, where V is the applied voltage between the anode and the cathode. As a result, if a particular electric field, $E_{\text{threshold}}$, is required for field emission from a cathode surface, then the required applied voltage is given by $V_{\text{threshold}} = E_{\text{threshold}} d$. From this expression, it is evident that the voltage required for emission is linearly dependent upon d, the distance between the anode and the sample (cathode).

For any given sample, a family of field emission I–V curves is recorded with each curve corresponding to a different anode-to-sample spacing. Due to the exponential nature of the field emission I–V curves, the 'turn-on' voltage or threshold voltage must be defined in terms of a specific current value. In this study, the voltage that results in a current value of 0.5 nA was chosen to represent the threshold voltage for electron emission. Each threshold voltage is then plotted vs. distance relative to the first I–V curve, and as expected, the resulting graph was linear. Upon fitting the data to a straight line, the slope represents the average field for the threshold current emission. This method for determining the average field does not rely upon the absolute anode to sample spacing, but rather an accurate measurement of the change in distance of the anode with respect to the sample. In addition, this technique has the advantage that the anode is never in contact with the sample.

3. Results

The goal of this work is to investigate issues associated with the measurement of field emission from nitrogen-doped diamond films. The focus is on high quality CVD diamond films which exhibit relatively low amounts of sp^2-bonded carbon. These films will exhibit highly insulating character and field emission measurements are complicated by this property.

To contrast the effects of the highly resistive nitrogen-doped films, several films were prepared with a high sp^2 content. These films were prepared in the same CVD chamber used for the deposition of the nitrogen-doped films grown for this study. The process conditions for these films were as follows: 10% methane in hydrogen, 900°C substrate temperate, 900 W micro-

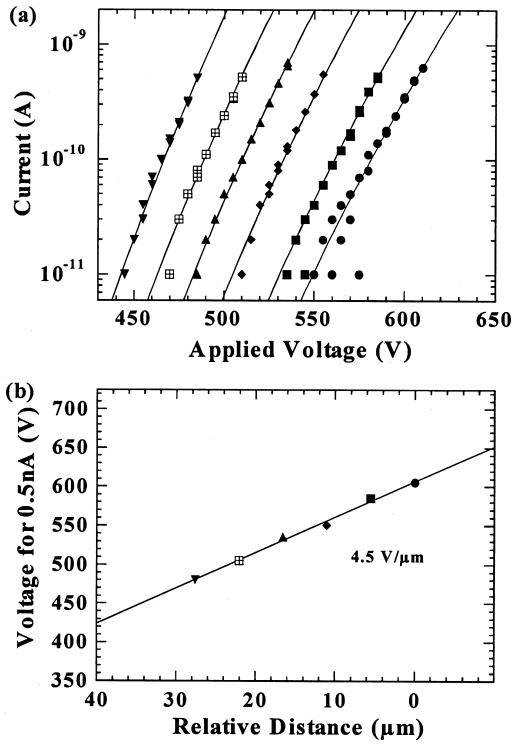

Fig. 1. Field emission measurements of a carbon film with high sp^2 content used to characterize the field emission testing system. Current–voltage measurements taken at several anode-to-sample distances are shown in (a). The threshold field vs. relative distance for this data set is shown in (b). The threshold fields required to obtain 0.5 nA of current are ~ 4 V μm^{-1}.

wave power, and 20 torr chamber pressure. After growth the samples were loaded directly into the field emission testing system without any surface pre-treatment. Fig. 1 illustrates the field emission data taken from one of the measurements. The sample exhibited field emission at exceptionally low fields, and there was no evidence of vacuum arcing that became a constant problem for the measurements of the high quality nitrogen-doped diamond films. The analysis of the I–V curves taken at several anode-to-cathode distances indicates that the threshold field required for 0.5 nA is ~ 4 V μm^{-1}. This value has been reproduced many times across the sample surface, as well as among several identically prepared samples. The emission mechanism for these high sp^2 containing carbon films is unclear and is a topic of ongoing research.

In this study a series of nitrogen-doped films were grown with gas phase [N]/[C] ratios from 0 to 48. The Raman spectra for all nitrogen-doped diamond films were obtained and have been reported previously [12]. In addition to the diamond Raman line at 1332 cm^{-1}, peaks associated with graphite at ~ 1350 cm^{-1} and ~ 1580 cm^{-1} are present in all spectra and become more prominent with increasing nitrogen content in the process gas. Other peaks from microcrystalline diamond and sp^2 bonding in diamond were also visible at 1140 cm^{-1} and ~ 1500 cm^{-1}, respectively [13]. At high nitrogen concentrations ([N]/[C] > 10), additional peaks are observed at 1190 cm^{-1} and 1550 cm^{-1}, which have been attributed to N–C complexes, are evident in the spectra, however, more work is necessary to determine their identity [14].

For gas phase [N]/[C] ratios from 0.1 to 1.0 and growth temperatures of ~ 900°C, nitrogen-doped diamond films can be deposited which exhibit PL bands attributed to nitrogen + vacancy optical centers. These bands are a characteristic of single substitutional nitrogen doping in diamond seen in type Ib HTHP synthetic diamond.

Without nitrogen addition, the diamond film morphology typifies high quality (i.e. low sp^2 content) diamond growth with well faceted grains. However, the addition of nitrogen degrades this faceting and ultimately produces extremely fine-grained diamond films at the highest nitrogen process gas concentrations [10].

Initially, several experiments were performed to evaluate the effect of nitrogen doping upon the threshold field required for electron field emission. However, these measurements produced widely varying and often irreproducible results. In fact, threshold fields for emission often varied between 9 V μm^{-1} and 80 V μm^{-1} for different regions on the same sample. Three field emission measurements on a nitrogen-doped film illustrating this instability are shown in Fig. 2.

It was only after the diamond surfaces were examined after field emission that the reason for this unstable behavior was evident. Micrographs of these surfaces revealed arc-damaged sites similar to features reported by Gröning et al. [15]. Despite refinements in the field emission measurements, micro-arcing was still observed for all films with [N]/[C] ratios less than 10. For these films, micro-arcing occurred during the first

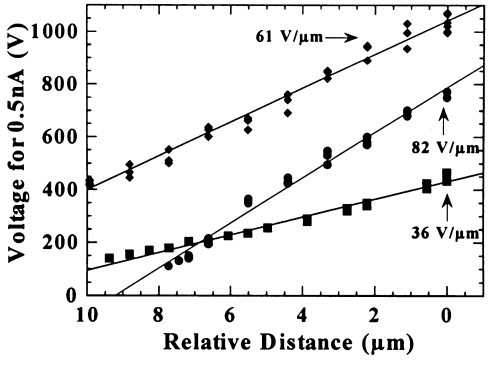

Fig. 2. Threshold voltage as a function of distance for a nitrogen-doped film in which arcing occurred during computer controlled auto-approach. The slope of each line represents the threshold field required for 0.5 nA of emission current. Each line represents a series of I–V measurements, which were taken at three different places near the center of the film.

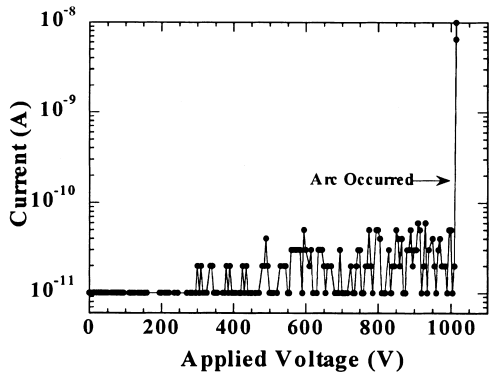

Fig. 3. Current–voltage curve during a field emission measurement in which an arcing event occurred. Note the discontinuous jump in the current at the end of the curve.

I–V measurement just after the current rose above the baseline noise level ($\pm 2 \times 10^{-11}$ A) in the test system. Micro-arcs are detected by monitoring the I–V curves for large discontinuous jumps in the measured current. Fig. 3 shows an I–V curve illustrating an arcing event. If field emission measurements are continued after micro-arcing, average threshold fields for electron emission again range from 9 to 80 V μm^{-1} depending upon the magnitude of the damage to the film and substrate. It is evident that measurements from arc-damaged surfaces are not indicative of the nitrogen-doped diamond film properties, but rather from the structurally changed material and/or sharp protrusions from the surface produced by the micro-arc.

For nitrogen-doped films with [N]/[C] $\geq$ 10, field emission could be observed without being preceded by an arcing event. Usually for these samples, approximately five I–V curves could be collected before an arcing event occurred. Analysis of data collected before arcing, indicate that the average threshold fields required for emission are 100–300 V μm^{-1}. After arcing, the threshold fields are again reduced to 9–80 V μm^{-1}. Fig. 4 shows the field emission data collected from a sample grown with [N]/[C] = 10. During this experiment an arc occurred at the end of the third I–V measurement. There is a distinct difference in the I–V curves collected before and after the arcing event. Both the shape and signal to noise ratio of the I–V curves change significantly after the arc indicating a change in the emission mechanism. As shown in Fig. 4c, analysis of the I–V data indicate that the threshold field required for emission before and after the arcing event is 250 V μm^{-1} and 73 V μm^{-1}, respectively. The effects that lead to the high threshold field in nitrogen-doped diamond have been discussed in a prior report [12]. Fig. 5 shows an SEM micrograph of the arc-damaged region from these measurements. EDS analysis of this region indicate that the irregular material on the surface is molybdenum from the anode.

4. Discussion

Despite the increase of structural defects and non-diamond phases observed in the Raman spectra upon the addition of nitrogen, photoluminescence measurements indicate single substitutional nitrogen incorporation. This means that these films possess the same nitrogen donor level observed in type Ib HPHT synthetic diamond single crystals. For thin diamond films, the concentration of substitutional nitrogen is difficult

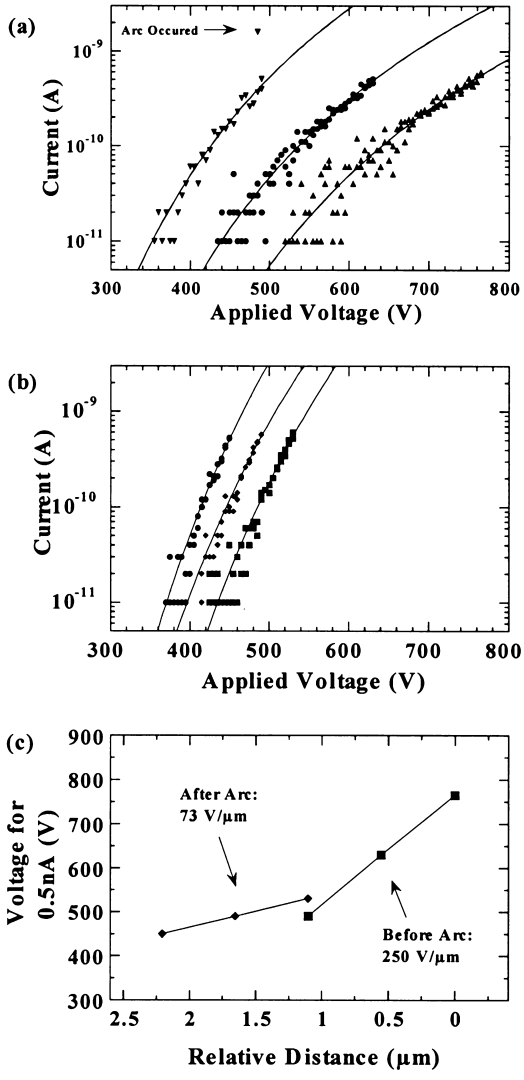

Fig. 4. Field emission measurements from a nitrogen-doped films grown on molybdenum with [N]/[C] = 10 in which an arc occurred during the measurements (the solid lines represent fits using the Fowler–Nordheim relation: $I = C_1 V^2 \exp(-C_2/V)$). Current–voltage measurements are taken at several anode-to-sample distances and are shown in (a) and (b). I–V measurements recorded before the arcing event are shown in (a). During the third I–V measurement an arc occurred. The I–V measurements taken after the arcing event are shown in (b). The threshold field analysis for this data set is shown in (c). The threshold fields required to obtain 0.5 nA of current before and after the arc are 250 and 73 V μm^{-1}, respectively.

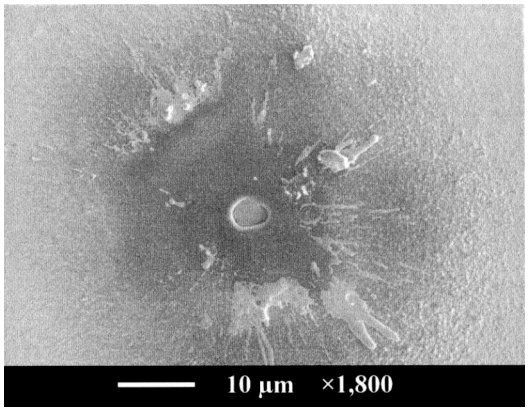

Fig. 5. Scanning electron micrograph of the arc-damaged region from the nitrogen-doped film shown in Fig. 4.

to quantify by analytical methods due the tendency for nitrogen to form aggregate defect centers and to collect at grain boundaries. We may estimate the nitrogen concentration in the diamond domains by comparison with other studies. The nitrogen concentration of homoepitaxial nitrogen-doped diamond films was investigated by Samlenski et al. using nuclear reaction analysis [16]. In that study, the nitrogen incorporation for the (100) and (111) growth sectors was $\sim 6.8 \times 10^{17}$ cm^{-3} and $\sim 2.3 \times 10^{18}$ cm^{-3}, respectively. As a result, the single substitutional nitrogen concentration of the films grown in this study is estimated between 10^{17} cm^{-3} and 10^{18} cm^{-3}. In comparison, the single substitutional nitrogen concentration found in type Ib HPHT single crystal is $\sim 10^{19}$ cm^{-3}.

The results presented here show that field emission is often preceded by micro-arcing for high quality nitrogen-doped CVD diamond films. This behavior is similar to that reported by Gröning et al. [15]. In that study, it was suggested that the localized pressure between anode and cathode increases due to electron stimulated desorption from electrons striking the anode [12]. Ultimately, a discharge occurs creating craters on the diamond surface. This model suggests that arcing would be a property of the anode material and not the cathode. However, our experiments have indicated that field emission can be obtained from carbon films with high sp^2 content without arcing. In addition with pressures less than 10^{-8} torr, one would expect that eventually all adsorbed species on the anode would be removed and the arcing behavior would cease. Our experiments have not indicated a decrease in arcing with time.

5. Conclusions

The objective of this work was to explore methods to measure field emission from high quality nitrogen-doped diamond films. The field emission properties of films with [N]/[C] gas phase concentrations up to 48 have been measured. In most cases detectable field emission is preceded by an arcing event that causes damage to the film and substrate and significantly changes the emission properties. Analysis of I–V data from the films that exhibit electron emission prior to arcing indicate that extremely high fields (100–300 V μm^{-1}) are required for field emission. It is likely that the required threshold fields for the samples that exhibit arcing before emission exceed 300 V μm^{-1}.

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