RELATIONSHIP OF FIELD EMISSION CHARACTERISTICS ON PROCESS GAS NITROGEN CONTENT IN NITROGEN DOPED DIAMOND FILMS

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ABSTRACT

This study explores the field emission properties of nitrogen doped diamond grown by microwave plasma CVD. Several diamond samples were grown on silicon under varying conditions. With certain process parameters, films can be grown which exhibit photoluminescence bands at 1.945eV and 2.154eV that are attributed to single substitutional nitrogen. Field emission characteristics were measured in ultrahigh vacuum with a position variable anode. For samples grown with gas phase [N]/[C] ratios less than 16, damage from micro-arcs occurred during the field emission measurements. Samples grown at higher [N]/[C] content could be measured without damage. These measurements indicate relatively high threshold fields (>100V/μm) for electron emission. From the data, two possible field emission mechanisms are presented. Conducting defect states in the bandgap of diamond may provide a source of electrons to the emitting diamond surface.

INTRODUCTION

In 1979 Himpsel *et al.* reported high quantum yield for photo-electron emission from the (111) hydrogen terminated surface of diamond [1]. Later it was determined that the (111) hydrogen terminated diamond surface exhibits a negative electron affinity (NEA) [2]. The presence of a NEA means that electrons in the conduction band can be freely emitted into vacuum. The combination of this NEA property along with extreme mechanical and chemical characteristics has made diamond a candidate material for cold cathode structures. The ideal cold cathode material would then exhibit a NEA and also sufficient *n*-type doping to supply electrons into the conduction band. To date however, it has proven difficult to produce *n*-type diamond.

Nitrogen has a high solubility in diamond and is found in both natural and synthetic diamonds. In synthetic diamond crystals, nitrogen is present in primarily single substitutional form with a donor level 1.7eV below the conduction band minimum [3]. Geis *et al.* have reported that a Schottky contact, which is formed when type Ib single crystal diamond is metallized with nickel, may be sufficient to supply electrons into the conduction band of diamond [4]. In this model the applied voltage drops primarily across the depletion layer. Electrons tunnel into the conduction band through the narrow Schottky barrier and are emitted into vacuum at the NEA surface. More recently Okano *et al.* have reported threshold fields less than 1V/μm for nitrogen doped diamond films grown by HFCVD using urea as a nitrogen doping source [5]. Despite these published reports, the mechanisms governing field emission from nitrogen doped diamond have not yet been determined.

This study explores the field emission properties of nitrogen doped diamond grown by microwave plasma CVD. These films were characterized by Raman scattering and photoluminescence spectroscopy. Field emission properties were measured with a position variable anode system. After field emission analysis, the surfaces were examined using optical and scanning electron microscopy (SEM).

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EXPERIMENT

Nitrogen doped diamond films were deposited in a commercially available ASTeX HPMS stainless steel microwave (2.45GHz) plasma CVD deposition chamber. *In situ* growth rate and film thickness information was monitored using laser reflectance interferometry (LRI). The conventional gas mixtures of hydrogen and methane were used as the growth precursors. Two sources of nitrogen were used depending on the desired nitrogen concentration in the process gas. For low nitrogen process concentrations a mixture of nitrogen (2.11%) diluted in hydrogen was used. For high nitrogen concentrations zero-grade nitrogen (99.998% minimum purity) was directly admitted to the process gas. With these two sources, nitrogen could be added as an impurity to the process gas with gas phase [N]/[C] ratios spanning from 0 to 80.

Polycrystalline diamond films containing nitrogen were deposited on 25mm diameter *n*-type ($1\Omega\cdot$cm) silicon substrates. In order to enhance nucleation, the substrates were hand polished for 10 minutes using 1-2μm diamond grit applied to a nylon polishing cloth. Following diamond grit polishing, the substrates were cleaned ultrasonically in acetone and methanol. Diamond nucleation was achieved at ~760°C surface temperature, 600W microwave power, 20Torr chamber pressure, and at a flow rate of 400sccm using process gases consisting of 2 vol.% methane in hydrogen. Nucleation time was determined by monitoring the LRI signal for an initial drop in intensity. For most samples the nucleation time was 21 minutes. Following the nucleation step the substrate temperature, microwave power, and chamber pressure were increased to the growth conditions.

Nitrogen doped diamond films were grown at substrate temperatures of ~900°C, 1300W microwave power, and 50Torr 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 500sccm. Nitrogen was only added to the process gas during the growth step. Following deposition, the nitrogen doped diamond films were characterized by micro-Raman spectroscopy, photoluminescence, optical microscopy, scanning electron microscopy (SEM), and field emission measurements.

The micro-Raman and PL spectra were recorded at room temperature with an ISA U-1000 scanning double monochromator using the 514.5nm line of an argon ion laser as the excitation source. The laser beam was focused on the samples to a spot size of ~3μm diameter using an Olympus BH-2 microscope.

The samples were examined using a Olympus BX60 microscope with magnifications up to 500x to identify large surface defects and/or damage both before and after field emission measurements. To evaluate the diamond film morphology and to distinguish smaller damage resulting from field emission measurements, the diamond thin films were imaged with a JEOL 6400 field emission SEM.

Field emission measurements were obtained in an ultra-high vacuum (UHV) environment with pressures typically $< 1\times10^{-8}$Torr. A cylinder of molybdenum (3mm or 1mm 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 >5mm) to minimize edge effects. The anode is mounted on a stage that is coupled to a UHV stepper motor. One step of the motor corresponds to a movement of the anode by 55nm. Current-voltage measurements are acquired with a computer controlled Keithley 237 Source Measure Unit (SMU). The SMU has the ability to simultaneously source a voltage and measure a current. A current limiting circuit is also included within the SMU so that no voltage is applied that causes the current to exceed 1×10^{-8}A.

In any given measurement, a family of I-V curves is recorded with each curve corresponding to a different anode to sample spacing. Initially, the anode is positioned at some unknown distance above the sample. The stepper motor count is recorded and an I-V curve is collected.

Next, the anode is moved closer to the sample by a known distance and the cycle is repeated until at least 5-10 curves are collected. As expected, the current-voltage curves shift to lower voltage values with decreasing distance. Because of the nature of the Fowler-Nordheim I-V equation, the "turn-on" voltage or threshold voltage must be defined in terms of a specific current value. The voltage that results in a current value of 0.5nA was chosen to represent the threshold voltage for electron emission. In order to prevent micro-arcs, it was necessary to limit the currents to below 0.5nA. Next each threshold voltage is plotted versus 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 the change in distance of the anode with respect to the sample.

RESULTS

The goal of this work is to investigate the role of nitrogen doping on the field emission properties of diamond. Field emission results from intrinsic and *p*-type diamond films have indicated lower threshold fields for samples with higher defect densities as measured by Raman scattering spectroscopy [6]. As a result, our efforts were to produce high quality nitrogen doped films, and not to deliberately deposit highly defective films. Despite this objective, as will be seen below, adding nitrogen to the process gas directly effects the resulting film quality. In this study two series of samples were grown. Series A were deposited with gas phase [N]/[C] ratios from 0 to 1, while for series B the gas phase [N]/[C] ratios ranged from 8 to 48. For [N]/[C] ratios greater than 48, no deposition is observed and the silicon substrates are visibly roughened. Results from these two series are presented below.

Raman scattering spectra for the series A and B are shown in figures 1 and 2, respectively. The addition of low quantities of nitrogen leads to a decrease in diamond film quality. Raman peaks associated with graphite at $\sim$1350cm^{-1} and $\sim$1580cm^{-1} are present in the spectra and become more prominent with increasing nitrogen content in the process gas. Other peaks from microcrystalline diamond and sp^2 bonding in diamond are also visible at 1120cm^{-1} and 1500cm^{-1}, respectively. As the nitrogen content in the process gas is increased to higher concentrations in series B, other features are present in the Raman spectra. Most notably is the presence of two

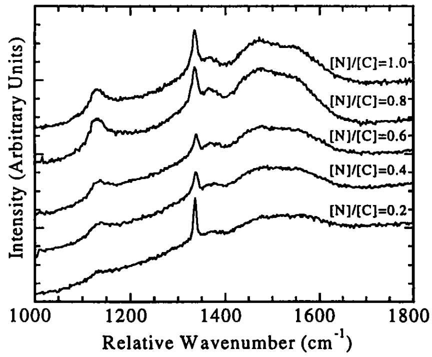

Figure 1. Raman spectra for diamond films grown with [N]/[C] gas phase ratios from 0.2 to 1.0.

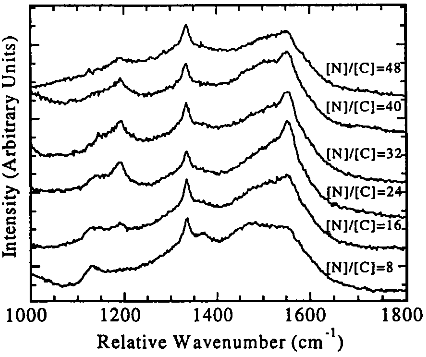

Figure 2. Raman spectra for diamond films grown with [N]/[C] gas phase ratios from 8 to 48.

peaks at 1190cm^{-1} and 1550cm^{-1}. One possible origin of these peaks may be from N-C complexes in the films, although more work needs to be performed to determine their identity [7]. The peaks associated with graphite, sp^2 bonding in diamond, and microcrystalline diamond are all reduced in intensity as the nitrogen addition is increased in this sample series.

For low gas phase [N]/[C] ratios, 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. The PL spectra for several nitrogen doped diamond samples exhibiting this luminescence is shown in figure 3. These nitrogen-related bands are found at 1.945eV and 2.154eV. Nitrogen addition to the process gas also seems to enhance the 1.680eV band that has been attributed to silicon incorporation in diamond films.

Field emission measurements for series A and B were obtained using the position variable anode as described above. For nitrogen doped samples with [N]/[C] ≤ 16, no electron emission could be detected prior to an arcing event. After arcing, emission was detected and average threshold fields from 20-70V/μm have been measured. Following field emission characterization, the surfaces of these diamond films were examined using optical and scanning electron microscopy. Figure 4 is a optical micrograph of a damaged region of a nitrogen doped film caused by micro-arcs during field emission testing. From the extent of the damage to the diamond/substrate, it is likely that the measured emission is not representative of the diamond film, but rather from features protruding from the flat surface. For nitrogen doped diamond films with [N]/[C] > 16, electron emission was detected without micro-arcing. These results indicate average threshold fields from 150 to 300V/μm. Lower threshold fields were obtained for films with higher [N]/[C] ratios. Field emission data from the sample with the lowest average field for current emission is shown in Figure 5. Figure 6 is a Fowler-Nordheim plot of the data shown in Figure 5. The linearity of the data indicate that the emission exhibits Fowler-Nordheim characteristics.

DISCUSSION

The objective of this work as stated earlier was to grow high quality nitrogen doped diamond films and to determine the role of nitrogen in these films. However as seen above, the diamond

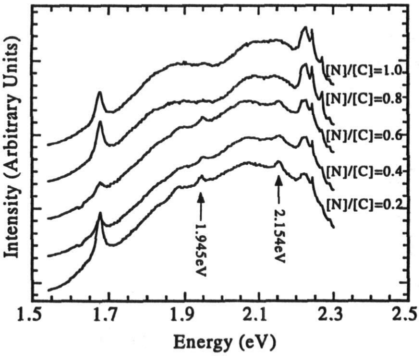

Figure 3. Photoluminescence spectra of diamond films grown with [N]/[C] gas phase ratios of 0.2 to 1.0.

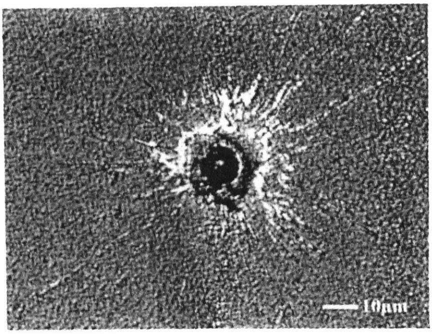

Figure 4. Optical micrograph of damaged diamond surface at 1000X after micro-arcing had occurred during field emission testing.

film quality is diminished by even small nitrogen concentrations in the process gas. The field emission properties of films with [N]/[C] gas phase concentrations up to 48 have been measured. Often the diamond films are damaged by micro-arcs during field emission characterization. It is likely that the observed emission is directly from the silicon substrate at points of damage. However, more work needs to be performed to clarify the role of damage in these films. A possible explanation for this behavior could be that the nitrogen is completely compensated by defects. The resulting film in which the nitrogen atoms do not participate electrically would act like a simple dielectric. Two possible models for electron emission from these materials are shown in Figure 7. In both models the field is dropped across vacuum and the nitrogen doped diamond with the field in the film reduced by the dielectric constant. In Figure 7a, electrons in the silicon tunnel into the conduction band of the diamond and are emitted into vacuum. In Figure 7b, electrons are emitted from conducting defect states located in the bandgap at the fermi level. At this point it is unclear which mechanism correctly describes the field emission process from these films. Energy analysis of the electrons emitted from these films may help identify the appropriate process.

CONCLUSIONS

Nitrogen-doped diamond films have been deposited on silicon substrates by microwave plasma CVD using nitrogen gas as the doping source. Photoluminescence spectra indicate single

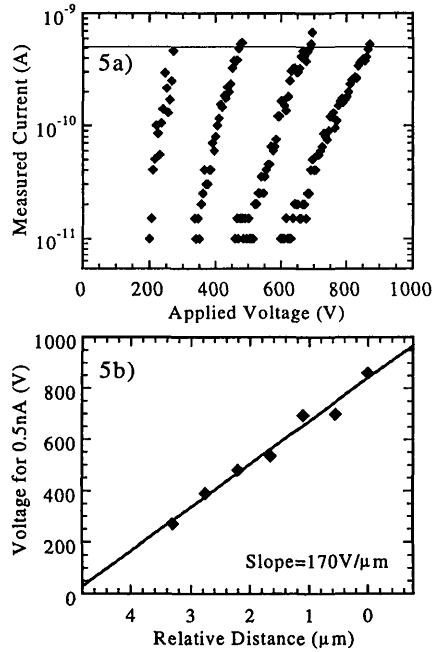

Figure 5. Field emission measurements of a nitrogen doped diamond film obtained at various anode to sample distances (a), and an analysis of the average field required to obtain an emission current of 0.5nA (b). The slope of the plot in (b) is 170V/μm.

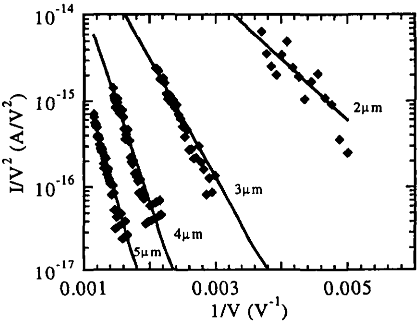

Figure 6. Fowler-Nordheim plot of the field emission data shown in Figure 5. The distances shown in the figure are determined from the average threshold field calculated in Figure 5.

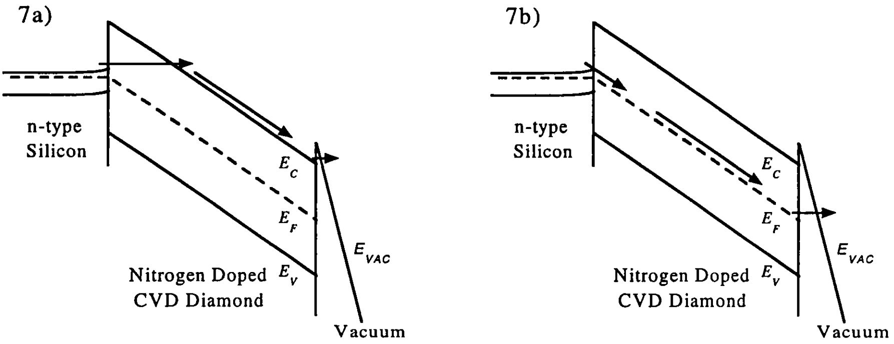

Figure 7. Possible models describing field emission from nitrogen doped diamond. In (a) electrons tunnel into the conduction band of diamond and are emitted into vacuum. In (b) electrons are emitted at the fermi level through defect states in the bandgap of diamond.

substitutional nitrogen doping for samples grown with [N]/[C] gas phase ratios of 0.1 to 0.8. However, for these films, electron emission could not be measured until an arcing event occurred. For samples grown with [N]/[C] greater than 16, emission was detected without being preceded by micro-arcing. We suggest that electrons are supplied from the silicon substrate to the emitting surface by conducting defect states within the bandgap.

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