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Growth, Characterization and Device Development in Monocrystalline Diamond Films

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13. ABSTRACT (Maximum 200 words) Nitrogen(N)-doped diamond(C) thin films were grown on Si(100) substrates using N/C gas ratios from 0 to 1:1, microwave plasma CVD and a three-step growth process involving biased enhanced nucleation (BEN). Micro-Raman spectra indicated that the film quality degraded with increasing N. The PL luminescence intensity increased with higher N/C ratios. UPS spectra indicated that thin N-doped films with N/C=1:5 exhibited an NEA surface. Field emission energy distribution (FEED) measurements were performed on diamond-coated Mo tips under ultra high vacuum conditions to investigate the origin of field emitted electrons. Mo emitters were prepared by electrochemical etching and were subsequently coated with diamond powder by a dielectrophoretic procedure. Field emission energy spectra were taken on the same samples before and after diamond coating. <i>In vacuo</i> thermal annealing of coated samples was essential to obtain stable field emission. Field emission energy distribution data indicate that the field emission current originated from the diamond/vacuum interface, and that electrons were emitted from the conduction band minimum of diamond.				
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I. Introduction

Diamond as a semiconductor in high-frequency, high-power transistors has unique advantages and disadvantages. Two advantages of diamond over other semiconductors used for these devices are its high thermal conductivity and high electric-field breakdown. The high thermal conductivity allows for higher power dissipation over similar devices made in Si or GaAs, and the higher electric field breakdown makes possible the production of substantially higher power, higher frequency devices than can be made with other commonly-used semiconductors.

In general, the use of bulk crystals severely limits the potential semiconductor applications of diamond. Among several problems typical for this approach are the difficulty of doping the bulk crystals, device integration problems, high cost and low area of such substrates. In principal, these problems can be alleviated via the availability of chemically vapor deposited (CVD) diamond films. Recent studies have shown that CVD diamond films have thermally activated conductivity with activation energies similar to crystalline diamonds with comparable doping levels. Acceptor doping via the gas phase is also possible during activated CVD growth by the addition of diborane to the primary gas stream.

The recently developed activated CVD methods have made feasible the growth of polycrystalline diamond thin films on many non-diamond substrates and the growth of single crystal thin films on diamond substrates. More specifically, single crystal epitaxial films have been grown on the {100} faces of natural and high pressure/high temperature synthetic crystals. Crystallographic perfection of these homoepitaxial films is comparable to that of natural diamond crystals. However, routes to the achievement of rapid nucleation on foreign substrates and heteroepitaxy on one or more of these substrates has proven more difficult to achieve. This area of study has been a principal focus of the research of this contract.

At present, the feasibility of diamond electronics has been demonstrated with several simple experimental devices, while the development of a true diamond-based semiconductor materials technology has several barriers which a host of investigators are struggling to surmount. It is in this latter regime of investigation that the research described in this report has and continues to address.

In this reporting period, (1) nitrogen doping of diamond films have been grown via microwave plasma CVD and a three-step growth process involving biased enhanced nucleation to produce electron emitting surfaces and (2) field emission energy distribution (FEED) measurements were performed on annealed diamond coated Mo tips under ultra high vacuum conditions to investigate the origin of field emitted electrons. The following sections are self-contained in that they present an introduction, the experimental procedures, results and discussion, summary and indications of future research for the given research thrust.

II. Incorporation of Nitrogen in Microwave Plasma CVD Diamond for Cold Cathode Device Applications

A. Introduction

Due to their unique combination of electrical and physical properties, diamond thin films have shown promise for use in electron field-emitting devices or cold cathode applications. Diamond surfaces which exhibit negative electron affinity (NEA) are particularly suitable for cold cathode structures due to their low barriers to electron emission. In contrast to conventional materials, the extreme hardness and chemical stability of diamond should exhibit minimal degradation with cathode operation. Recent field emission reports have shown that nitrogen doped diamond films have exhibited turn-on fields as low as $0.5 \text{ V}/\mu\text{m}$. However, the mechanisms controlling emission and the role of nitrogen are still unclear. In addition, nitrogen doped diamond has exhibited high electron energy emission when high voltages (1-10 kV) are applied to the diamond. It is unclear whether the voltage drop is across the bulk diamond or near the emitting surface. This report outlines the status of nitrogen incorporation in microwave plasma CVD diamond films and its influence on the properties of the films.

B. Experimental Procedure

The 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. A mixture of nitrogen (2.11%) in hydrogen was used as the nitrogen source. During film growth, nitrogen was added as an impurity to the process gas with gas phase N/C ratios ranging from 0 to 1:1. Polycrystalline diamond films containing nitrogen were grown on 25 mm diameter n-type silicon substrates. A three-step growth sequence employing biased enhanced nucleation was used to clean the substrate, form initial diamond nuclei, and grow out the polycrystalline diamond films. Nitrogen was only added to the process gas during the growth step as shown in Table I.

The substrate temperature was measured using a one-color optical pyrometer in the center of the sample. The film growth rate and thickness was monitored *in situ* using laser reflectance interferometry using the 632.8 nm line from a He-Ne laser at normal incidence and a Si photodiode as the photodetector.

The nitrogen doped diamond films were characterized using micro-Raman spectroscopy, photoluminescence (PL), and ultraviolet photoemission spectroscopy (UPS). UPS spectra were measured as-loaded and after a H-plasma exposure. The UPS studies were performed in an integrated ultra high vacuum transfer system. The system capabilities include individual chambers for hydrogen plasma processing and UPS.

Table I. Experimental Conditions for Growth of Nitrogen Doped Diamond Films

	Pretreatment	Nucleation Step	Growth Step
Microwave Power	600 W	600 W	1300 W
Chamber Pressure	20 Torr	20 Torr	50 Torr
Substrate Temperature	~745 °C	~755 °C	~800 °C
H ₂ Flow	400 sccm	400 sccm	723 sccm
CH ₄ Flow	0 sccm	8.00 sccm	4.13 sccm
N ₂ /H ₂ mixture Flow	0 sccm	0 sccm	varies (0-100 sccm)
Substrate Bias	grounded	-200 V	grounded
Time	10 minutes	~15 minutes	15 min - 8 hrs

The micro-Raman and PL spectra were recorded at room temperature with an ISA U-1000 scanning double monochromator using the 514 nm line of an argon ion laser as the excitation source. The laser beam was focused on the samples to a spot of ~3 μm diameter using an Olympus BH-2 microscope.

The UPS chamber has a base pressure of 2×10^{-10} Torr. Operating conditions involve pressures up to 1×10^{-9} Torr, but the higher pressure is due to the helium inflow and does not contaminate the sample. The UPS system utilizes a helium resonance lamp (the He I line) to provide a source of 21.2 eV light. Photoemitted electrons are measured with a 50 mm mean radius hemispherical electron analyzer operated at a 0.15 eV energy resolution and a 2° angular resolution. The analyzer (VSW HA50) is mounted on a double goniometer and can be tilted with respect to the sample in two independent directions. The nitrogen doped diamond samples were fastened by tantalum wire to a molybdenum sample holder. The sample holder is biased up to 4 V to allow low energy electrons to overcome the work function of the analyzer. The Fermi level of the system (sample and analyzer) is determined by UPS measurement of the sample holder with no sample bias (i.e., grounded).

The hydrogen plasma system has a base pressure of 1.0×10^{-9} Torr but operates in the milli-Torr range of pressure. In these experiments, 82 sccm of hydrogen was admitted into the plasma chamber. This hydrogen flow rate results in an operating pressure of 25 mTorr. Power is coupled into the chamber through rf induction. The rf power used was 20 watts. The samples face the plasma and are located at ~40 cm from the edge of the rf plasma. The samples were annealed at 450°C during plasma exposure using a tungsten filament located in close proximity behind the sample. The samples were exposed for one minute to the H-plasma.

C. Results and Discussion

The first part of this work focused on determining the extent that nitrogen can be incorporated into microwave plasma CVD diamond films. Films were grown with N/C ratios

ranging from 0:1:1 to a thickness of ~ 1 micron as determined from LRI data. Micro-Raman spectroscopy was used to determine the effect of varying the nitrogen content in the process gas upon the crystalline quality of the diamond films. Figure 1 shows the micro-Raman spectra of the nitrogen doped diamond films with varying gas phase N/C ratios. The Raman signature due to the diamond at 1332 cm^{-1} decreases while the broad peak centered around 1500 cm^{-1} due to non-diamond carbon increases with increasing N/C. The FWHM of the 1332 cm^{-1} peak also increases from 7 cm^{-1} for N/C=0 to over 14 cm^{-1} for N/C=1:1. These results indicate that the addition of nitrogen to the process gas degrades the crystalline quality of the diamond films. It is not clear at this point if it is the incorporation of nitrogen at these high concentrations which causes the declining film quality or if it is gas phase reactions which inhibit high quality diamond growth.

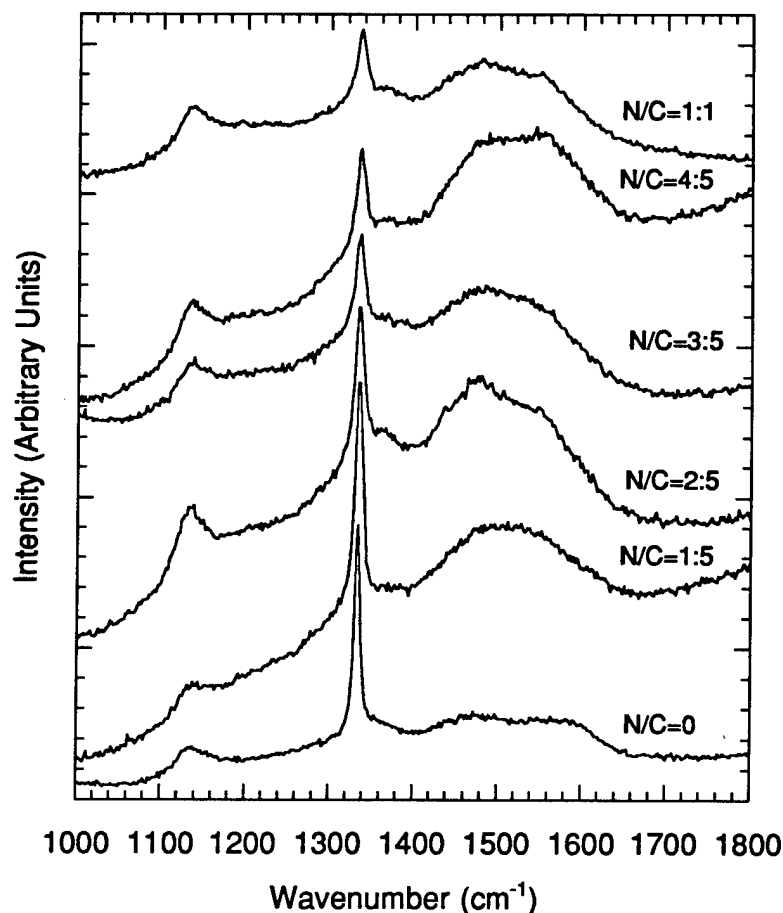


Figure 1. Micro-Raman spectra of nitrogen doped diamond films with varying gas phase N/C ratios.

Photoluminescence spectra were obtained to determine whether nitrogen was being incorporated into the films and to establish which nitrogen related defects were present in the

films. The PL spectra of the diamond films with varying N/C ratios are shown in Fig. 2. These spectra show that the addition of nitrogen greatly increases the overall photoluminescence intensity. In addition for N/C=1:5 there is a large increase in the 1.68 eV band which has been attributed to an optical transition in a Si complex center. One explanation for this increase in this defect center is that with N/C=1:5 there is an enhanced silicon etch mechanism resulting in more silicon in the film. An alternative view is that the 1.68 eV band is somehow also related to the amount of nitrogen in the films. Unfortunately, detailed analysis of the PL spectra is difficult with this data due to the broad nature of the bands which lie between the 1.68 eV band and the superimposed Raman peaks. The nitrogen related bands at 2.154 eV and 1.945 eV are not easily distinguishable from the background luminescence. Low temperature PL measurements using the 457.9 nm argon laser line will be required to fully characterize these samples.

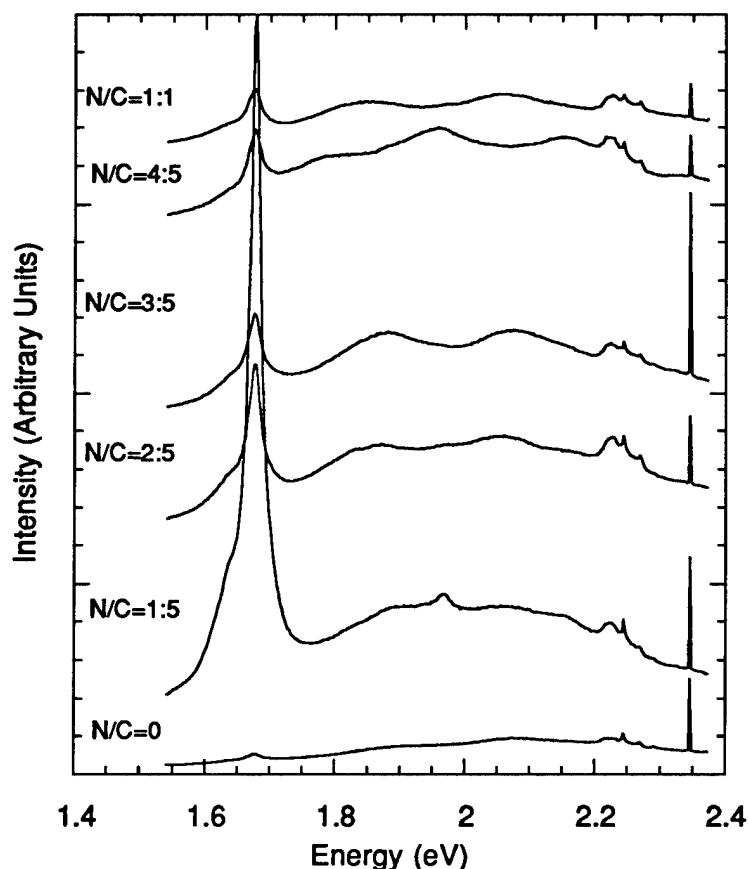


Figure 2. Photoluminescence spectra of nitrogen doped diamond films with varying gas phase N/C ratios.

Several thin nitrogen doped films with N/C=1:5 were grown for UPS characterization. The film thickness ranged from 1000 Å to 3000 Å to minimize charging effects. The UPS spectra of a 1000 Å film is shown in Fig. 3. UPS spectra were obtained before and after H-plasma

exposure. The onset of emission is found to shift ~ 2 eV after H-plasma exposure. This is due to the removal of surface adsorbates which pin the Fermi level. In addition, this film exhibits an NEA surface as determined by the indicative shape and width of the spectra. An interesting note is that the total width of the spectra is larger than anticipated for the 21.2 eV He I excitation source assuming a bandgap of 5.45 eV for the diamond film. There are two separate possibilities which we are considering to explain this phenomenon. First, there could be emission from states below the conduction band minimum. This could be from H-induced states or possibly exciton-related emission. A more likely explanation for the increase in width is that there is an inhomogeneity of the surface Fermi level due to multiple crystalline domains. At this point it is difficult to exclude the possibility that there is some charging occurring in the film. More work needs to be performed before the exact location of the Fermi level can be determined with respect to the valence band. However this data suggest that the Fermi level is located ~ 2.00 eV above the valence band.

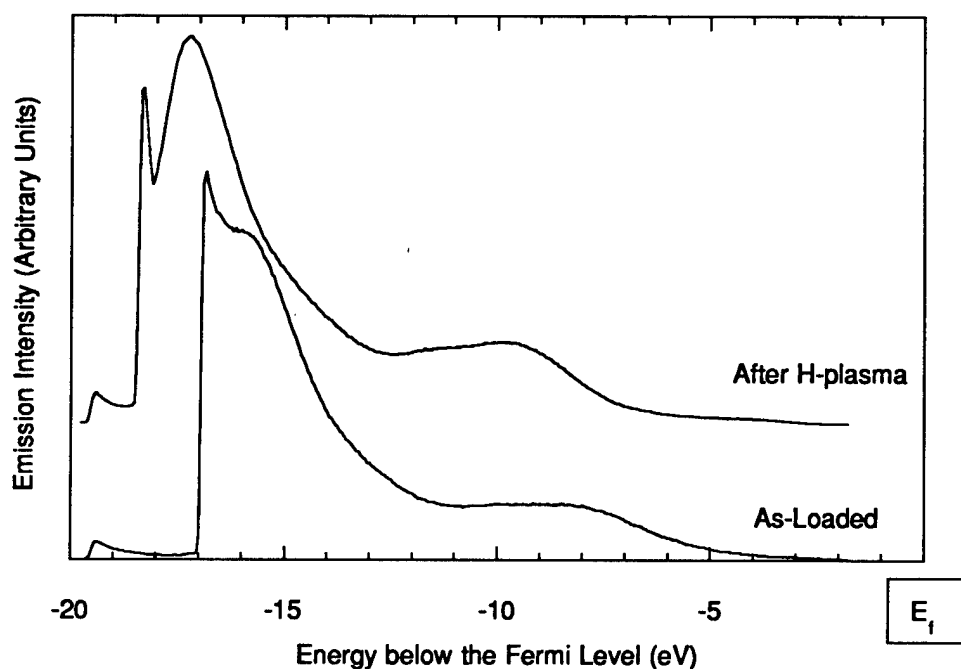


Figure 3. UPS spectra of ~ 1000 Å nitrogen doped diamond film with N/C=1:5 before and after H-plasma exposure.

D. Future Research Plans and Goals

The work outlined in this report represents work in progress and there are many experiments and issues which remain to be addressed. In particular, there are plans to increase the gas phase N/C ratios to the point that the diamond growth is completely degraded. In addition other nitrogen sources such as ammonia or urea may be used to increase the nitrogen doping

efficiency at lower gas phase N/C ratios. With these samples it will be necessary to utilize low temperature measurements to characterize the photoluminescence spectra. These spectra may be used to determine if nitrogen is incorporated substitutionally or interstitially. Most importantly, field emission measurements will be performed to establish the dependence of the I-V characteristics upon the nitrogen content in the films. Additionally field emission measurements as a function of the film thickness will be measured to give better insight to mechanisms involved with electron emission from these samples. UPS will be used to determine if there is a dependence of the existence of an NEA with the N/C ratio. UPS will also be used to establish whether the Fermi level moves toward the conduction band with increased nitrogen doping. Finally, high voltage experiments will be performed to determine if high energy electron emission occurs with these nitrogen doped films.

III. Energy Distribution of Field Emitted Electrons from Diamond-Coated Molybdenum Tips

A. Introduction

An increasing interest in vacuum microelectronics, and primarily in flat panel display devices, has recently stimulated research on microstructured field emitters. Molybdenum micro-field emitters have already been demonstrated in the late 1960s[1], and their performance has continuously been improved throughout the past three decades[2, 3]. In order to meet the requirements of potential applications and to alleviate the reported problem of cathode sputtering by self-generated positive ions[4], lowering of the required operating voltage of field emission devices has been identified as a primary goal in ongoing research. Stable coating materials with low work functions have, therefore, become of highest interest. Diamond is an interesting coating material due to its large thermal conductivity, its chemical stability, and the negative electron affinity (NEA) behavior of its H terminated (111)[5] and (100)[6] surfaces. *I-V* characterization data on diamond coated Mo field emitters have been published recently[7] and demonstrate a considerable enhancement of the field emission current, as compared to uncoated Mo tips. The emission mechanism, however, has not yet been studied thoroughly. In this section, we report on field emission energy distribution (FEED) measurements that have been performed to help clarify the physical mechanisms governing the field emission process from Mo/diamond emitters.

B. Experimental Approach

Single Mo emitter tips were made from Mo wire (diameter: 0.125 mm) and were sharpened by electrochemical etching in a concentrated KOH solution (applied voltage: 10 V DC, counterelectrode: Pt). Typical radii of curvature of the sharpened Mo tips were less than 100 nm. Diamond coatings were deposited subsequently by a dielectrophoretic procedure, which consisted of dipping a positively-biased (ca. 10 V) Mo tip into an ultrasonically-prepared suspension of diamond powder (typical particle size: 100 nm) in ethanol. Due to dipolar interaction with the nonuniform external electric field, the electrostatically neutral, suspended diamond particles moved toward regions of higher field strength and were thus deposited on the Mo tip. Careful timing of the coating procedure allowed deposition of diamond layers with a thickness of a few hundred nanometers. The diamond powder used was nominally undoped; Raman spectroscopy of the diamond powder evidenced no Raman active defects. The shape of the pure Mo tips, as well as the thickness and uniformity of the dielectrophoretic coatings, was monitored by Scanning Electron Microscopy (SEM), before and after the Field Emission Energy Distribution (FEED) experiments.

Field emission energy distribution experiments were carried out using a test device that consisted of a tip holder facing an electrically insulated, metallic gate with a circular opening

(diameter: 500 μm). A tip was mounted at a distance of 500 μm from the gate, and was aligned with the gate opening using a stereo-microscope. Measurements were performed in a UHV analysis chamber (pressure: 10^{-9} Torr), where the test device was aligned with the entrance lens system of a hemispherical electron analyzer (VG Instruments CLAM II) used to record the energy distribution of the field emitted electrons that passed through the gate opening. The gate was kept at ground potential, while a negative bias voltage was applied to the tip.

C. Results and Discussion

In a first step, FEED spectra were taken from uncoated Mo tips, after *in vacuo* desorption at 450°C for 1h. Figure 1 shows a typical FEED spectrum obtained from a bare Mo tip where the count rate, which is proportional to the field emission current j , is displayed as a function of the energy loss $E = V_o - E_{kin}$, with V_o denoting the potential applied between the gate (+) and tip (-), and E_{kin} the kinetic energy of the emitted electrons. The theoretical dependence of $j(E)$ is given in a free electron approximation by[8]

$$j(E) = \frac{e\pi(2m)^{1/2}f(E)}{\hbar^3 (-E)^{1/2}} \exp\left(-\frac{4}{3} \left(\frac{2m}{\hbar^2}\right)^{1/2} \frac{(-E)^{3/2}}{eF}\right), \quad (1)$$

where e and m denote the charge and mass of the electron, respectively, F is the electric field at the emission site, and $f(E) = (1 + \exp(E - E_f)/kT)^{-1}$ the Fermi-Dirac distribution at a temperature T , set to $T = 300\text{K}$ in the following. Taking into account the finite resolution of the electron spectrometer, modeled by a Gaussian instrument function

$$i(E) \sim \exp(-4 \ln^2(E/\Delta E_{FWHM})^2), \quad (2)$$

the experimental data were fitted to the convolution $j(E) \otimes i(E)$. Fit parameters were the field enhancement factor, $\beta = F/V_o$, the work function of Mo $\phi_{Mo} = E_f$, the full width at half maximum of the instrument function, ΔE_{FWHM} , as well as a factor linking the observed count rates to the calculated field emission current j . This factor took into account that a portion of the emitted electron current did not pass through the gate, and that the electron analyzer captured only part of the angular distribution of the emitted beam.

Field emission energy distribution data collected from several Mo tips at applied voltages in a range from 500 to 900 V consistently yielded work functions of $\phi_{Mo} = (4.2 \pm 0.2)$ eV, and field enhancement factors in the order of $\beta \approx 10^5 \text{ cm}^{-1}$; both values are in good agreement with previous I - V characterization data of similar tips[7]. The width of the analyzer instrument function was determined to be $\Delta E_{FWHM} = (0.47 \pm 0.06)$ eV at an analyzer pass energy of 20 eV.

In a second step, the same Mo tips were coated with diamond powder and annealed *in vacuo* at 600°C for 1 h. All samples showed a lowered “turn-on” voltage for field emission,

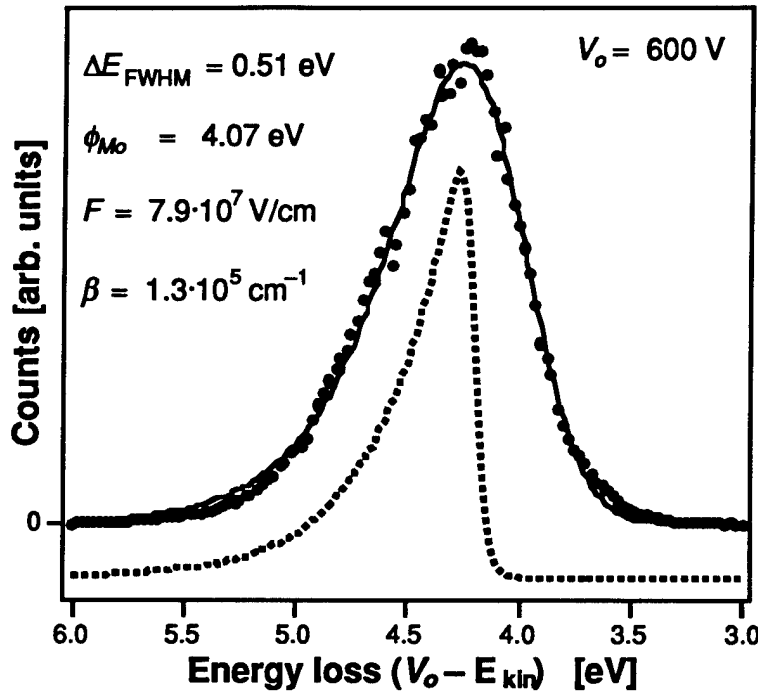


Figure 1. FEED spectrum of a Mo tip prior to coating. Experimental data are fitted to a theoretical FEED spectrum (Eq. (1)), convolved with a Gaussian instrument function. The dashed line shows the calculated free electron FEED spectrum without instrument broadening. Analyzer pass energy: 20 eV.

and, in contrast to the bare Mo tips, the energy of the emitted electrons became dependent on the applied voltage. Figure 2 shows two field emission spectra of a diamond coated Mo tip recorded at applied voltages of 400 V, and 600 V, respectively. Only one single peak was observed, and its position was found to follow a linear dependence on the applied voltage V_o , as shown in Fig. 3. The energy of the emitted electrons was well defined, as the full width at half maximum of the recorded spectra (typically 0.6 eV) was only marginally broader than the analyzer's resolution ($\Delta E_{\text{FWHM}} = 0.5$ eV). Broadening of the spectra by an additional 0.3 eV was observed at the highest applied voltages.

The observed linear increase of the energy loss with the applied voltage can be explained by a model taking into account the voltage drop across the dielectric diamond coating (see Fig. 4). Electrons are injected from the Fermi level E_f of the Mo tip into the conduction band of diamond where they settle close to the conduction band minimum (CBM). The observed emission originates from the diamond/vacuum interface, where the original vacuum level (VL) is lowered by a voltage drop ΔV , proportional to the applied voltage V_o and the thickness of the layer, and inversely proportional to the dielectric constant ϵ of the layer material. Extrapolation of the data shown in Fig. 3 toward $V_o = 0$ yields an energy loss of 1 eV, which,

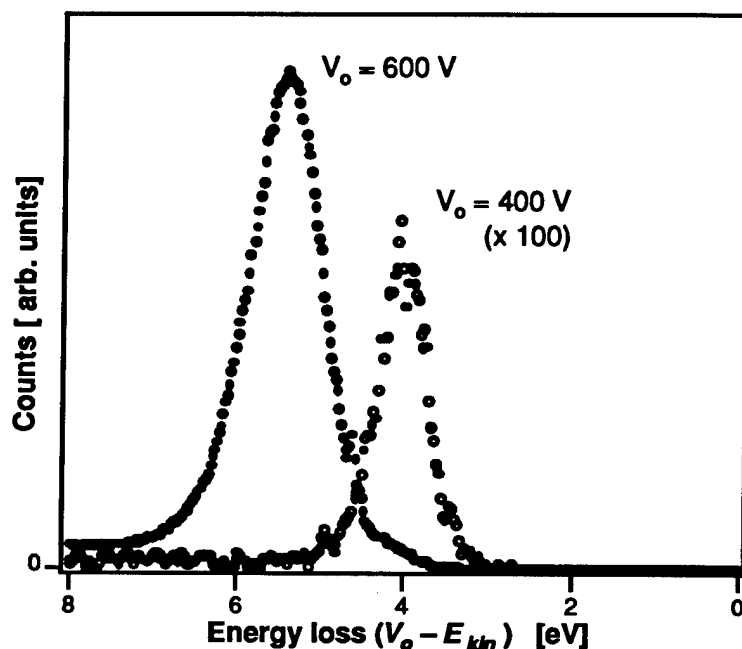


Figure 2. FEED spectra of a diamond coated Mo tip, taken at applied voltages of 400 V, and 600 V. Analyzer pass energy: 20 eV.

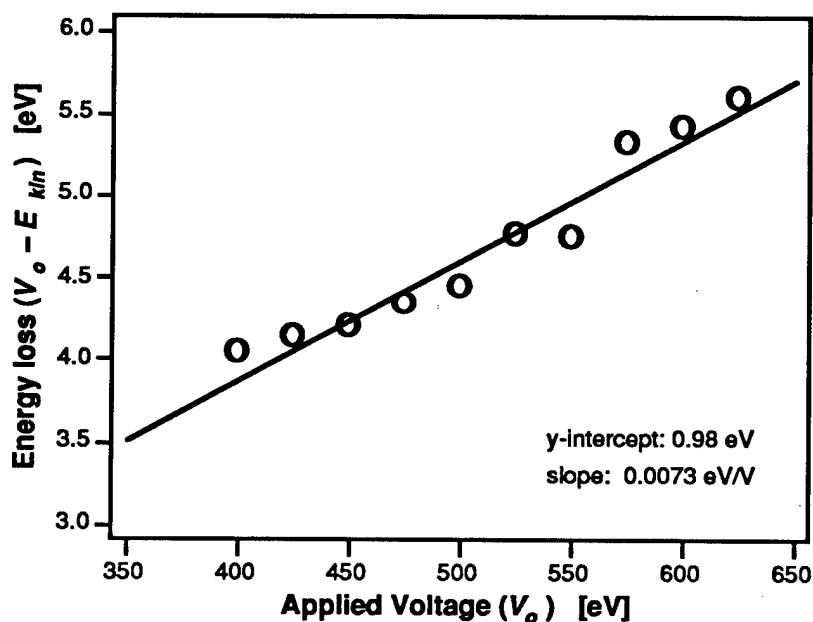


Figure 3. FEED peak positions of a diamond coated Mo tip vs. applied voltage. Energy loss of emitted electrons increases linearly with applied voltage.

within this model, is identified as a positive electron affinity $\chi_{\text{dia}} \approx 1$ eV. The fact that no electrons were emitted at energies above the Fermi level of the underlying Mo tip supports the proposed electron injection mechanism, while the minor peak broadening with applied voltage indicates a fast thermalization process to the bottom of the conduction band.

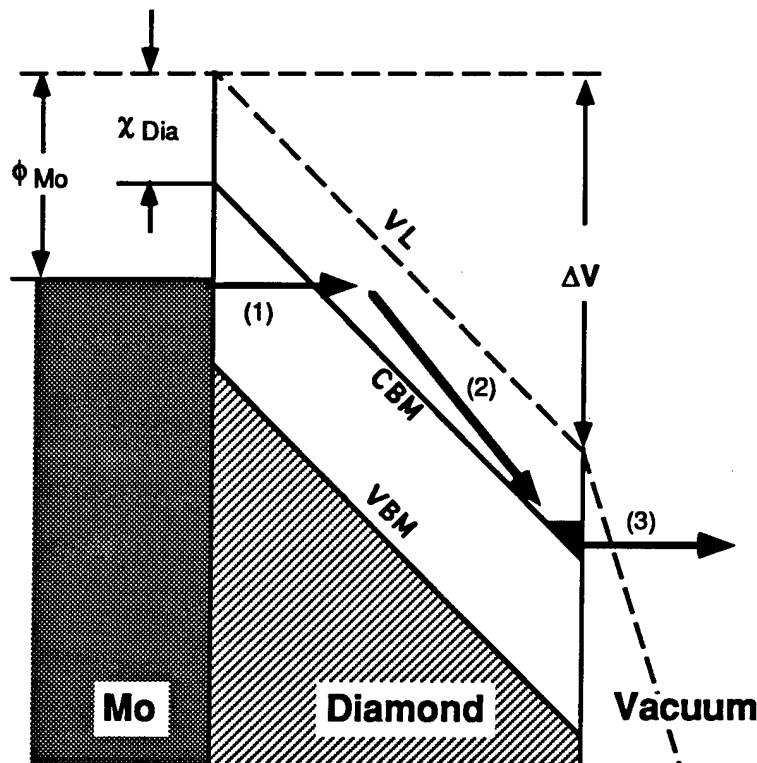


Figure 4. Simplified band diagram illustrating the field emission mechanism from a diamond coated Mo emitter. Electrons are injected (1) from the Mo/diamond interface into the conduction band of diamond, where they settle (2) to the conduction band minimum (CBM). Field emission (3) takes place from the conduction band minimum at the diamond/vacuum interface. Lowering of the vacuum level ΔV at the emission site is due to a voltage drop across the dielectric diamond layer and is proportional to the applied voltage.

In contrast to recently published FEED data[9] obtained from a natural *p*-type diamond sample, we did not observe field emission from the valence band maximum (VBM) in the case of nominally undoped diamond powder. We believe that sufficiently large hole conduction is a mandatory requirement to obtain considerable valence band field emission.

All of the data presented here were collected from annealed samples. Prior to annealing, field emission currents from diamond coated Mo tips were unstable, and FEED spectra showed more complex features that are under current investigation. The annealing process presumably improved the conductivity between the diamond layer and the Mo surface by formation of a conductive Mo_2C layer[10].

D. Conclusions

In conclusion, we have developed a simple model describing field emission from diamond coated Mo tips, based on experimental FEED results. Field emission occurs from the conduction band minimum of diamond at the diamond/vacuum interface; due to a voltage drop

across the dielectric diamond layer, the energy of the emitted electrons depends linearly on the applied voltage. In our study, we did not observe ballistic or partially thermalized electrons which were both speculated to contribute to the emission process. Additionally, undoped diamond features no field emission from its valence band due to missing hole conductivity.

E. Acknowledgments

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IV. Distribution List

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