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Surface cleaning, electronic states and electron affinity of diamond (100), (111) and (110) surfaces

P.K. Baumann [1], R.J. Nemanich *

Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA

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Abstract

The effects of cleaning natural type IIb diamond (100), (111) and (110) samples by annealing and hydrogen – or deuterium plasma exposure were investigated by means of ultraviolet photoemission spectroscopy (UPS). Different wet chemical cleaning processes (a conventional chromic acid clean and an electrochemical etch) and a H plasma exposure have been employed to clean natural type IIb semiconducting diamond C(100) wafers. The effects of these processes on the diamond surface have been assessed and compared. As evidenced by Auger electron spectroscopy (AES), an oxygen free surface could be obtained following vacuum annealing to 900°C for the electrochemical process compared to 1050°C for the chromic acid etch. In addition, the technique of atomic force microscopy demonstrated the presence of oriented pits on the surface of samples that were electrochemically etched for long times at high currents. After a H plasma exposure the negative electron affinity (NEA) peak in the UPS spectra doubled in intensity. An anneal to 1100°C resulted in the removal of the sharp NEA feature. A second H plasma treatment resulted in the reappearance of the NEA peak similar to that after the first H plasma exposure. A (2×1) reconstructed low energy electron diffraction pattern was observed subsequent to the anneals as well as the H plasma treatments. The fact that a NEA can be induced or removed repeatedly by means of a H plasma exposure or annealing at 1100°C, respectively, provides evidence to correlate the appearance of a NEA with the presence of a monohydride terminated surface. Corresponding effects were found for (111) and (110) surfaces. A NEA could be induced by a H plasma and removed by annealing at 900 or 800°C for diamond (111) or (110) surfaces, respectively. Following a deuterium plasma exposure the diamond surfaces exhibited a NEA like the ones treated by a hydrogen plasma. Higher annealing temperatures were necessary to remove the NEA for deuterium due to the isotope effect. Values of 79 and 81 V μm^{-1} were measured for the field emission threshold of the oxygen terminated C(100) and C(110) surfaces, respectively. A value of 25 V μm^{-1} was determined for the hydrogen terminated C(110) surface.

Keywords: Diamond; Electron emission; Field emission; Photoemission; Semiconductor surfaces; Surface electronic phenomena; Ultraviolet photoelectron spectroscopy

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1. Introduction

The electron affinity of a semiconductor is defined as the energy difference between the vacuum level and the conduction band minimum. For most materials the vacuum level lies above the conduction band minimum, corresponding to a positive electron affinity. Surfaces of wide bandgap semiconductors like diamond have the potential of exhibiting a negative electron affinity (NEA) since the conduction band minimum lies near the vacuum level to begin with. Electrons present in the conduction band have sufficient energy to

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[1] Present address: Materials Science Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA. E-mail: peter_baumann@qmgate.anl.gov

* Corresponding author. Fax: (+1) 919 5157331; e-mail: Robert_Nemanich@ncsu.edu

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overcome the work function of a NEA surface and can be emitted into the vacuum. Indeed, different surface terminations can shift the position of the bands with respect to the vacuum level and, therefore, induce a NEA or remove it [1–5]. These changes have been found to be due to surface adsorbates. Different surface adsorbates result in changes of the surface dipole. Changing the surface dipole can lead to an increase or decrease in the electron affinity. For example hydrogen has been reported to induce a NEA on the diamond (111) and (100) surfaces. Whereas oxygen leads to a dipole such that a positive electron affinity is observed on these surfaces [1–5].

One aspect that contributes to the dipole is the electronegativity of the adsorbing species. However, the surface dipole may not only result from the differences in electronegativity between C and H or C and O, but also the symmetry of the charge distribution at the site. Robertson [6] pointed out that both hydrogen and oxygen sites on the diamond surface are asymmetric, and this should lead to additional dipole effects and thus affect the electron affinity. The lone pair orbitals of oxygen extending from the surface are expected to increase the work function. Similarly, an adsorbate free surface would exhibit dangling bonds resulting in a dipole of the same polarity as for an oxygen terminated surface. In contrast, a hydrogen layer on the surface results in a dipole such that the work function is reduced.

The surface cleaning and following processing steps will directly affect the surface termination of the diamond and, therefore, affect the electron affinity. In this study, several common surface preparation techniques are employed to clean different surfaces of natural diamond samples, and the electronic structure and electron affinity of the surfaces are measured. In particular, the study focuses on the role of oxygen or hydrogen termination in comparison to the adsorbate free surface.

Different wet chemical cleaning methods have been employed to remove non-diamond carbon and metal impurities from the diamond surface. One approach includes immersion in boiling chromic acid and aqua regia. Another is electrochemical etching to remove conductive surface layers [7]. It has been shown that either procedure is capable of removing non-diamond carbon [7,8]. Following both approaches the diamond surfaces were found to be covered with oxygen. To remove these contaminants vacuum cleaning steps such as annealing or plasma exposure can be used.

Oxygen termination on the C(100) surface has been reported to lead to a (1×1) structure [9]. Two possible bonding configurations have been proposed for the oxygen terminated surface [10]. In one an oxygen atom is double-bonded to a carbon atom, or, alternatively, an oxygen atom could form a bridge between two adjacent carbon atoms. Both structures are consistent with a (1×1) low energy electron diffraction (LEED) pattern. In contrast, a (2×1) reconstruction has been observed following annealing at 900–1000°C or a H plasma exposure [9]. Also, these surfaces were found to exhibit a NEA [9]. The (2×1) structure and the NEA are indicative of a monohydride termination. In the presence of atomic hydrogen, a (2×1) monohydride structure has been found to be the most stable according to theoretical studies [9]. Furthermore, for the (2×1) reconstructed surface ab initio calculations determined a NEA for a monohydride terminated surface and a positive electron affinity for a surface free of adsorbates.

As-loaded diamond C(111) samples have been reported to be at least partially covered with a monohydride. The monohydride terminated surfaces show a (1×1) unreconstructed LEED pattern. Also a NEA was detected for these samples experimentally by ultraviolet photoemission spectroscopy (UPS) [1–5]. Zhang et al. [11] deduced a value of -1.56 eV for the electron affinity from pseudo potential calculations. Annealing these surfaces to above 950°C leads to a (2×1) reconstruction, and a positive electron affinity is observed. These changes are attributed to the removal of hydrogen. An Ar plasma clean was found to have the same effects on the electron affinity [5].

The clean diamond C(110) surface has been reported to exhibit a (1×1) LEED pattern [4,12–14]. However, there has been considerable difficulty in obtaining a high quality (110) surface [15]. Pate et al. observed only washed out photoemission spectra from the (110) surface and attributed this to a poor quality (110) surface [13]. The desorption of hydrogen from the C(110) surface has been addressed in several studies. Using photon stimulated ion desorption, Pate found a significant reduction in hydrogen on the (110) surface at 800°C [4]. By means of ionization loss spectroscopy, Pepper reported changes in the electronic structure at 850–900°C that were attributed to hydrogen desorption from the surface [16]. Employing multiple internal reflection infrared spectroscopy, McGonigal et al. determined that the C–H stretching mode on a (110) surface vanished for annealing temperatures between 800 and 900°C [17]. This effect has been associated with the desorption of hydrogen. But hydrogen desorption has been reported up to 1050°C [4] from a C(110) surface.

Deuterium terminated C(100) surfaces have been examined by Francz and Oelhafen [18] by means of UV photoemission spectroscopy. A weak low energy feature indicative of a NEA was detected for a deuterium exposed (100) surface. UPS spectra of the clean surface were found to exhibit a peak at 1.5–2.0 eV below the Fermi level. This peak was reduced following deuterium exposure. As determined by means of X-ray photoemission spectroscopy (XPS), deuterium could be desorbed from C(100) surfaces at 1177°C [19]. Using time-of-flight scattering and recoil spectroscopy, Koleske et al. have studied the abstraction of hydrogen and deuterium from polycrystalline diamond surfaces [20]. The rate of H abstraction of D was determined to be about one-third the rate found for D abstraction of H. This result was attributed to differences in momentum transfer for the two isotopes.

Photoemission spectroscopy is a very sensitive method to determine whether a surface exhibits a NEA or to measure the positive electron affinity. The incident light excites electrons from the valence band into states in the conduction band. Some of these electrons quasi-thermalize to the conduction band minimum. For NEA surfaces these secondary electrons may be emitted into vacuum and are detected as a sharp feature at the low energy end of photoemission spectra [4,21]. A careful measurement of the width of the photoemission spectrum can be used to determine if the low energy emission occurs from the conduction band minimum. However, for a positive electron affinity, emission from the conduction band minimum will not occur, and the value of the electron affinity can be deduced.

The field emission mechanism is more complex than the one for photoemission. Here carrier injection into the semiconductor, transport through the bulk as well as emission from the surface into vacuum have to be considered. Field emission measurements are performed by bringing a metal anode close to the sample surface and applying a bias between the two. The emission current is measured as a function of applied voltage.

In this study the effects of different wet chemical and in vacuo cleaning processes on diamond (100), (111) and (110) samples are analyzed in terms of surface structure, chemistry, morphology and electron emission.

2. Experimental

The ultra high vacuum (UHV) system employed in this study consists of several interconnected chambers including systems used for annealing, H plasma cleaning, UPS, LEED and Auger electron spectroscopy (AES). Samples can be moved between the chambers by a rail mounted UHV transfer system.

Natural type IIb single crystal semiconducting diamond (100), (111) and (110) samples ($3.0 \times 3.0 \times 0.25$ mm) were used in this study. The samples were purchased from Dubbeldee Harris Corp. The semiconducting wafers were necessary since undoped samples showed charging and did not yield a signal. The resistivity of the samples was typically ca 10^4 Ωcm. The samples were commercially polished using 0.1 μm diamond grit. The experiments were performed with diamond samples of the respective orientation: (100), (111) or (110). Most experiments were repeated and in some cases different samples of the same orientation were used. In all instances equivalent results were obtained.

Prior to loading the samples into the UHV system the samples were cleaned by either electrochemical etching [6], or the more commonly used acid etching. The electrochemical etching process involved applying a d.c. bias of 350 V between two Pt electrodes that were placed in deionized (DI) water as an electrolyte. The sample was suspended in water between the two electrodes. The surface of the sample that was to be cleaned of non-diamond carbon and metal contaminants was positioned to face the cathode. A constant current of ca 0 5 mA was measured, and a typical etching lasted 2 h. Following the electrochemical etching residue was detected and a HF dip was employed to remove the residue from the surface [8]. To examine the effect of different wet chemical etches on the surface properties, some diamond (100) samples were cleaned by a chromic acid etch. This cleaning step involved immersing the samples for 15 min in boiling chromic acid (CrO_3:H_2SO_4) to remove non-diamond carbon. This was followed by boiling for 15 min in aqua regia (3HCl:1HNO_3) to remove metal contaminants. Finally the samples were rinsed in DI water. After each of the two cleaning processes the samples were blown dry with N_2 gas, mounted on a molybdenum holder and transferred into the UHV system. This system consists of several chambers that are interconnected with a transferline. The transferline has a base pressure of 1×10^{-9} Torr. The base pressure in the chamber used for annealing and UPS measurements was 2×10^{-10} Torr.

As in vacuo cleaning steps the diamond (100) samples were annealed between 500 and 1150°C. An optical pyrometer focused on the Mo plate holding the sample was employed to measure the temperature during the anneals. The annealing caused the pressure to increase to between 8×10^{-10}–7×10^{-9} Torr during the various anneals.

Determination of the actual temperature of the diamond substrate presents a significant problem. Recently, Smentkowski et al. [22] have addressed this problem with a configuration very similar to the one employed in this study. In their study they measured the temperature inside a natural diamond type IIa wafer using a thermocouple which was placed inside a laser drilled hole in the diamond sample [22]. This temperature reading was compared to the temperature of the Mo holder onto which the diamond sample was mounted. The sample was held to the sample holder using W–Re wires. To achieve a steady state temperature of ~1130°C for the diamond wafer, it was necessary to heat the Mo holder to 1270°C or 140°C higher than the diamond. It was also reported that the temperature difference between the diamond and the Mo holder may be >350°C due to differences in mounting tension in the wires used to attach the diamond wafer onto the Mo holder [22].

Each of the experiments was repeated with different diamond samples to ensure that the measured desorption temperatures for oxygen, hydrogen and deuterium were consistent. Each of the measured temperatures was found to be reproducible, independent of the different diamond samples and mounting attempts. As a point of comparison, a value of 1250°C was found for deuterium desorption from a C(100) surface, and this value is somewhat higher than the value of 1177°C reported by Smentkowski et al. [19]. It is likely that this difference is just the temperature difference noted in the temperature calibration measurements. It is noted that the calibration experiments indicate a temperature difference of 140°C at this temperature. It is not possible to determine whether this smaller difference is due to the experimental configuration or the semiconducting character of the type IIb samples employed here. Since accurate calibration measurements were not completed, the temperatures quoted throughout this paper are those measured at the thermocouple.

The wafers were also cleaned with a H plasma. For this purpose the diamond crystals were heated to 500°C and exposed to a remotely excited rf H plasma. The details of the plasma chamber have been described previously [23]. During the plasma clean the H pressure was held at 50 mTorr.

To compare the effects of hydrogen and deuterium termination, diamond (100) and (110) samples were exposed to deuterium or hydrogen plasmas. Except for using a different gas the process parameters for either plasma were the same.

Following the different cleaning steps, UPS, LEED and AES were employed to analyze the surface properties. The photoemission was excited by He I (21.21 eV) radiation from a gas discharge

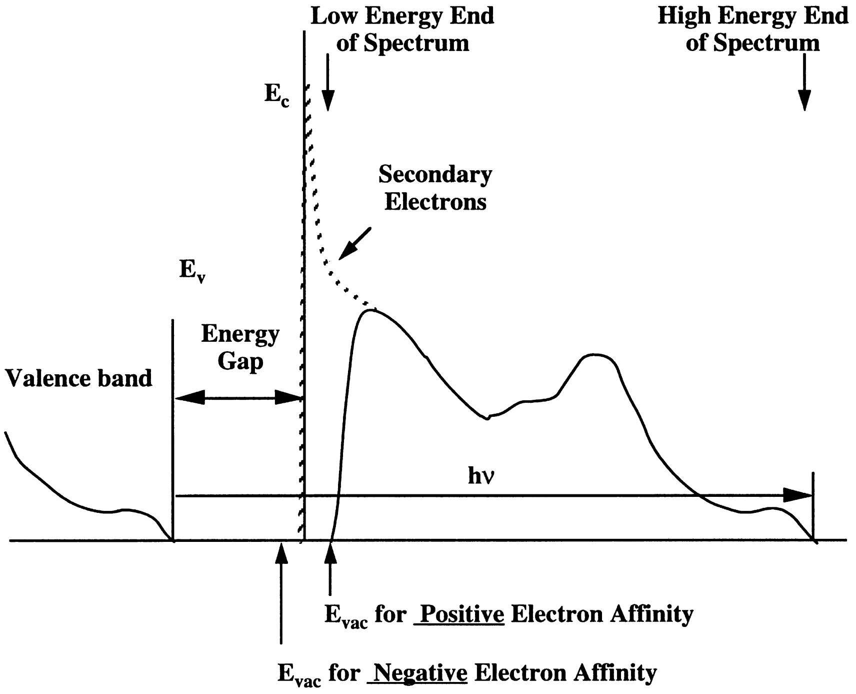


Fig. 1. Schematic diagram of photoemission spectra for a negative electron affinity surface (· · ·) and a positive electron affinity surface (———).

lamp. A 50 mm hemispherical analyzer was employed to detect the emitted electrons. The system had an energy resolution of 0.15 eV and an acceptance angle of 2°. To determine the Fermi level, UPS measurements were performed on reference samples of freshly deposited gold layers. A bias of 1 or 2 V was applied to the sample to overcome the work function of the analyzer and thus to detect the low energy electrons emitted from the NEA surface. The position of the sharp NEA peak at the low energy end of photoemission spectra corresponds to the energy position of the conduction band minimum, E_c (Fig. 1). It is noted that the NEA peak appears at the low kinetic energy end of the spectrum. Typical photoemission spectra are plotted versus binding energy relative to the Fermi level. In this case the low kinetic energy electrons are at the largest negative binding energy. In this paper the features from -15 to -17 eV binding energy will be referred to as low energy end. Emission from E_c appears E_v+E_G at in the spectrum, where E_v is the energy of the valence band maximum and E_o that of the bandgap. Emission from the valence band maximum is positioned at $E_v+h\nu$ in the spectrum. This is the high energy end of the spectrum. The spectral width or the distance between emission from the valence band maximum and the conduction band minimum is therefore $h\nu-E_G$. With the values for He I radiation $h\nu=21.21$ eV and the bandgap of diamond E_G 5.45 eV, a spectral width of ~15.7 eV is determined for a NEA surface. It can only be determined that the surface exhibits a NEA. However, the magnitude of the NEA can not be measured by UPS since there is no emission from states below the conduction band minimum. In comparison, for the case of a positive electron affinity surface, the low energy cutoff will be determined by the position of the vacuum level, and the spectral width will be smaller. Thus, the actual value of the electron affinity can be deduced from the position of the low energy end. This means the low energy cutoff will change in proportion to the change in magnitude of the electron affinity.

The field emission measurements were carried

Table 1
Summary of the UPS and on C(100), (111) and (110) surfaces

Surface				
	500°C	900°C	1100°C	
C(100) after chromic acid clean	PEA, $\chi=1.00$ eV	PEA, $\chi=0.70$ eV	NEA, $\chi<0$	
C(100) after electrochemical etch	PEA, $\chi=1.45$ eV	NEA, $\chi<0$	PEA, $\chi=0.75$ eV	
	900°C	H-plasma	1100°C	H-plasma
C(100)	NEA, $\chi<0$	NEA, $\chi<0$	PEA, $\chi=0.75$ eV	NEA, $\chi<0$
	1100°C	1250°C		
C(100) after H plasma treatment	PEA, $\chi=0.75$ eV	PEA, $\chi=0.75$ eV		
C(100) after D plasma treatment	NEA, $\chi<0$	PEA, $\chi=0.75$ eV		
	RT to 600°C	H-plasma	900°C	
C(111) after chromic acid clean or electrochemical etch	NEA, $\chi<0$	NEA, $\chi<0$	PEA, $\chi=0.5$ eV	
	700°C	800°C	H plasma	800°C
C(110)	NEA, $\chi<0$	NEA, $\chi<0.6$ eV	NEA, $\chi<0$	PEA, $\chi=0.6$ eV
	800°C	900°C		
C(110) after H plasma treatment	PEA, $\chi=0.6$ eV	PEA, $\chi=0.6$ eV		
C(110) after D plasma treatment	NEA, $\chi<0$	PEA, $\chi=0.6$ eV		
	Field emission threshold			
C(100) after electrochemical etch	79 V μm^{-1}			
C(110) after electrochemical etch	81 V μm^{-1}			
C(110) after H plasma treatment	25 V μm^{-1}			

RT, Room temperature; χ, electron affinity; PEA, positive electron affinity; NEA, negative electron affinity. Unless noted otherwise the surfaces have been cleaned by electrochemical etching. The experimental uncertainties are 0.1 eV. Also field emission results of C(100) and (110) and are shown.

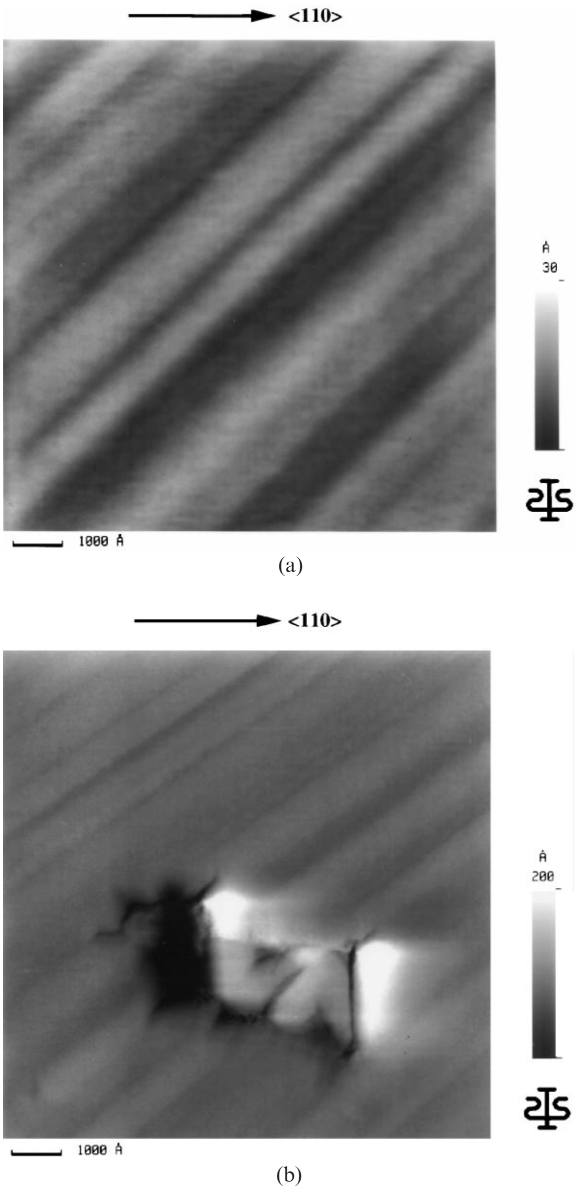
out in a vacuum chamber with a base pressure of $\sim 2\times10^{-8}$ Torr. A bias of 0–1100 V was applied between the sample and a 2 mm diameter stainless steel anode with a rounded tip. The *I–V* characteristics were measured using a Keithley 237 source-measuring unit. The distance between the sample and the anode could be varied in vacuum by a stepper motor. Typical distances were 2–30 μm. Measurements were obtained at a series of different distances.

3. Results

This section presents results which relate the cleaning procedure and the processing to the electron affinity. The results for all of the processes described are summarized in Table 1.

3.1. Comparison of chromic acid or electrochemical etches

As determined by atomic force microscopy (AFM) measurements, all of the samples used in this study exhibited parallel linear groves to each other with a depth of ~20 Å (Fig. 2a). These features are attributed to the polishing procedure of the supplier. The crystal orientation of the wafers has been determined by Laue X-ray measurements (provided by the supplier). Subsequent to a chromic acid etching no changes in surface morphology of the samples was observed. Even after the substrates had been boiled in chromic acid and aqua regia for 2 h each, no changes were detected in the AFM scans. Also, AFM images of crystals electrochemically etched for 2 h at 0.5 mA did not reveal any changes either. For one diamond (100) sample the duration of the electrochemical etching was extended to study possible effects on the morphology. Also, the current was increased. Following extended electrochemical etching of 12 h at 50 mA, scattered pits could be detected on the diamond surface. In fact it was determined that these etching pits were oriented along the ⟨110⟩ crystallographic directions (Fig. 2b). AES scans of these surfaces displayed larger peaks attributed to SiO_2. In a comparative experiment graphite and damaged amorphized diamond surface layers were removed by this electrochemical etch [8]. Based on these observations it is proposed that the etching pits actually mark the location of defects in the surface region of the diamond. Such defects may be a result from the polishing procedure or could also be intrinsic to the natural diamond crystals. In comparison, subsequent to extended chromic acid etching no etching pits were observed by means of AFM.



(a)

(b)

Fig. 2. AFM image of diamond (100) (a) following polish by supplier and (b) after electrochemical etching for 12 h at 50 mA. Etch pits oriented along the ⟨110⟩ crystallographic direction are detected.

Subsequent to either of the two wet chemical cleaning procedures, the as-loaded diamond (100) crystals exhibited a comparable unreconstructed (1 × 1) LEED pattern. Furthermore, AES spectra showed peaks indicative of the presence of oxygen on all samples. The AES of (100) surfaces after the two cleaning procedures are displayed in Figs. 3 and 4. In comparison, the amount of oxygen detected by AES on the diamond (100) surface treated by electrochemical etching and a HF dip, appeared to be somewhat less than that for the surface cleaned by the chromic acid etch. The

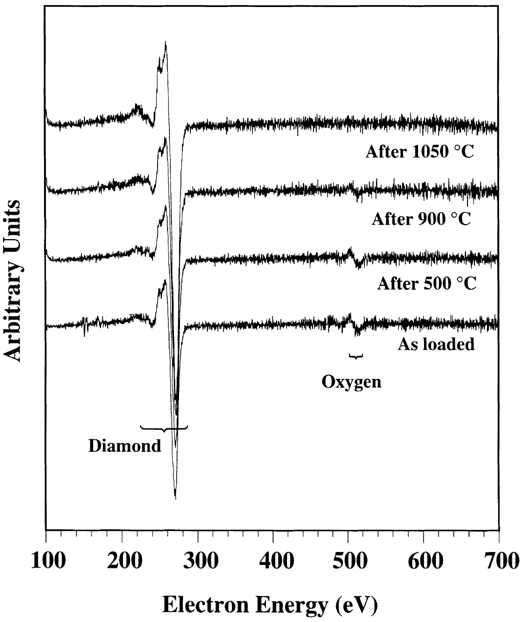


Fig. 3. Auger spectra of diamond C(100) following chromic acid clean as a function of annealing temperature. The as loaded surface exhibits features indicative of oxygen which can be reduced at 900°C and removed at 1050°C. A reconstructed (2×1) LEED pattern and a NEA were observed following annealing at 1050°C.

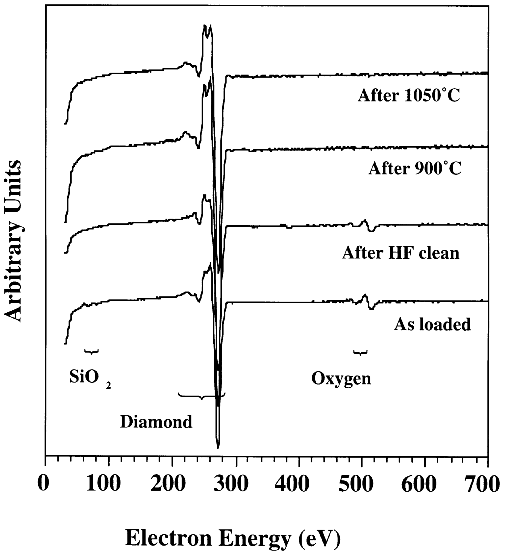


Fig. 4. Auger spectra of diamond C(100) following an electrochemical etch and HF dip as a function of annealing temperature. The as loaded surface exhibits features indicative of oxygen which can be removed at 900°C. A reconstructed (2×1) LEED pattern and a NEA were observed following annealing at 900 and 1050°C. These spectra show a lower noise level than for Fig. 3 since a different filament was used.

amount of oxygen was estimated to be at least a monolayer. No fluorine remnants were detected on the surface after the HF etch, but experiments to determine the sensitivity of AES for F terminated diamond surfaces were not carried out (to exclude the possibility of desorption due to the electron beam).

For both surfaces, annealing at 500°C did not remove a significant portion of the oxygen as detected by means of AES, indicating that most of the oxygen was chemisorbed. Upon heating to 900°C a reduction of the surface oxygen (Fig. 3) was observed for diamond substrates cleaned by employing chromic acid, but the surfaces remained in the (1×1) structure. Following an anneal to 1050°C the amount of oxygen on the surface dropped below the detection limit of the AES instrument. A reconstructed (2×1) LEED pattern appeared. For the (100) surface prepared with the electrochemical etch, after annealing to 900°C oxygen was no longer detected by AES. Again, the surface exhibited a (2×1) reconstructed structure.

Previous studies have shown the relationship of O termination and the electron affinity of the diamond (100) surface [9]. The width of the UPS spectrum of the surface increased with increased annealing temperature indicating a NEA at 1050°C and no detectable oxygen. In the experiments presented here, similar effects were observed for the (100) surface prepared by an electrochemical etch, only the NEA is observed after annealing to 900°C. The UPS of the electrochemical etched surface annealed to 900°C is shown in Fig. 5. In addition to the increased width of the spectrum, a sharp low energy peak positioned at the conduction band minimum was detected in the UPS spectra. Upon heating to 1050°C neither the AES spectrum nor the LEED pattern changed, and the NEA surface was retained. The results indicate oxygen desorption and the observation of a NEA at a lower temperature than for the (100) surface prepared with a chromic acid etch.

Several (111) surfaces were prepared with the

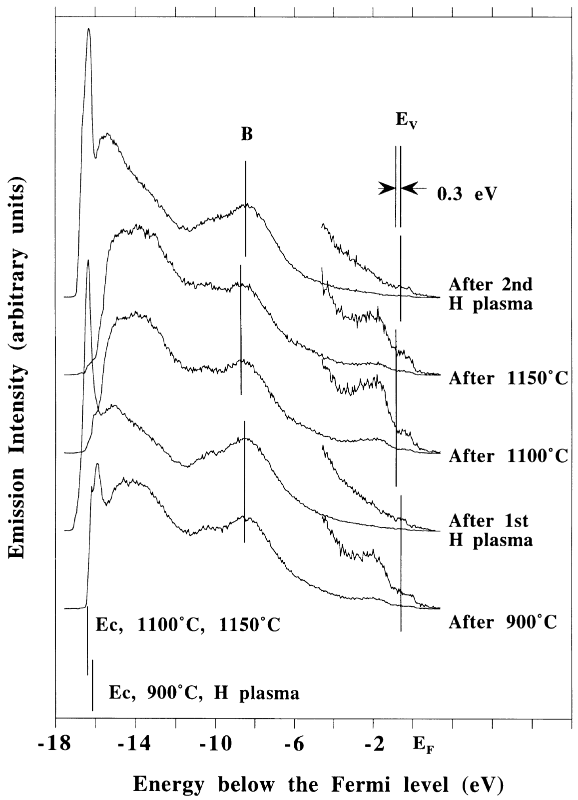


Fig. 5. UV photoemission spectra of a diamond (100) surface cleaned by means of electrochemical etching. The sequence of spectra follows from bottom to top: annealing at 900°C, first hydrogen plasma, annealing at 1100°C, 1150°C second hydrogen plasma. Note that the sections of the spectra around E_V and E_F have been blown up by a factor of 5.

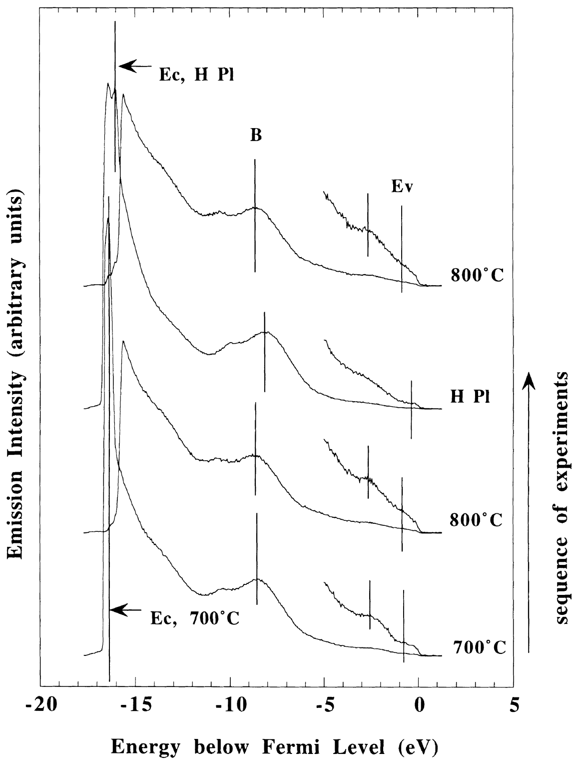


Fig. 6. UV photoemission spectra of a diamond (110) surface. A NEA was observed following annealing at 700°C. Annealing at 800°C removes the NEA. The NEA can be induced and removed again by hydrogen plasma exposure and annealing at 800°C, respectively. The sections of the spectra close to E_V and E_F have been magnified five times.

electrochemical etching procedure. Most of the as-loaded diamond samples exhibited a positive electron affinity, however, a few displayed a sharp low energy peak in the UPS spectra indicative of a NEA. Annealing to 600°C resulted in a NEA for all of the (111) surfaces studied.

The as-loaded (110) samples exhibited features indicative of oxygen in the AES spectrum. Also a positive electron affinity was observed by means of UPS. Subsequent to annealing the (110) samples to 700°C, a (1 × 1) LEED pattern was observed, and the oxygen concentration on the surface dropped to below the detection limit of the AES instrument. The low energy cut off of the UPS spectrum shifted to lower energies (Fig. 6), indicating a reduction of the electron affinity. In addition, a sharp low energy peak attributed to a NEA appeared.

3.2. Hydrogen plasma exposure

Exposing the annealed (100) surfaces to a H plasma resulted in about double the intensity for the NEA peak. The results for the surface prepared with electrochemical etching are shown in Fig. 5. Emission extending to 0.3 eV below the conduction band minimum was observed. Annealing at 1100°C resulted in the removal of the sharp NEA peak and a shift of the low energy end by 0.5 eV to higher energies. As evidenced from the position of the strong feature labeled “B”, the entire spectrum shifted by 0.3 eV to lower energies. The low energy end still exhibited a small shoulder that was removed after annealing at 1150°C. This small shoulder may be due to some hydrogen remnants on the surface following annealing at 1100°C. A feature positioned at 1.2 eV below the valence band maximum was detected subsequent to annealing at 900, 1000 and 1150°C. (Due to shifts in the spectra, this peak appeared at 1.8 eV below the Fermi level following annealing at 900°C and at 2.1 eV below the Fermi level after annealing at 1100 and 1150°C.)

A H plasma exposure resulted in a NEA for the (111) surface which could be removed by subsequent annealing at 950°C. Diamond (111) surfaces cleaned by chromic acid etching have been examined previously [5]. This reference also reports that a peak positioned 1.2 eV below the valence band maximum was detected following annealing at 950°C. As far as can be told from the authors' and previous [5] experiments the properties of the diamond surfaces following either one of the two wet chemical cleaning processes did not differ significantly. It has been reported previously that as-loaded diamond (111) samples may be at least partially terminated with a monohydride [4,5].

For the (110) surface prepared by an electrochemical etch, annealing at 800°C removed the sharp NEA feature, and the width of the spectrum was reduced by 0.7 eV. Only for one (110) surface studied was a (2 × 1) LEED pattern observed. The other (110) surfaces showed a (1 × 1) LEED pattern. All these surfaces exhibited equivalent UPS spectra. In particular, at the high energy end of the spectra a feature positioned at 1.8 eV below the valence band edge appeared following annealing at 700 or 800°C (Fig. 6).

Exposing the (110) surfaces to a H plasma also resulted in the re-appearance of the NEA characteristics. In addition, the peak located at 1.8 eV below the valence band edge was reduced significantly (Fig. 6). Following a H plasma exposure a (1 × 1) LEED pattern was found for all the (110) surfaces studied. Annealing at 800°C ensured the NEA could be removed again. And the peak at 1.8 eV below the valence band edge reappeared. The characteristics of the high energy end of the spectrum observed subsequent to annealing at 700°C appeared to be between those detected following annealing at 800°C and those observed after a H plasma exposure. A second H plasma clean resulted in a UPS spectrum similar to that obtained after the initial H plasma. The LEED pattern remained reconstructed (2 × 1). But the secondary spots were again lower in intensity after the second H plasma clean.

3.3. *Effects of deuterium plasma exposure*

Deuterium plasma exposure at a temperature of 500°C resulted in the removal of oxygen from the diamond (100) and (110) samples, as shown by AES. Also, a (2 × 1) LEED pattern was detected for C(100) and a (1 × 1) structure for C(110). These effects are equivalent to the case of a hydrogen plasma. Following a deuterium plasma clean the diamond surfaces exhibited a NEA like the surfaces treated by a hydrogen plasma. However, differences in the thermal stability were found between deuterium versus hydrogen on diamond surfaces.

While the NEA attributed to hydrogen termination of diamond (100) surfaces could be removed by annealing at 1100°C, the NEA was still observed after annealing deuterium terminated diamond (100) surfaces to 1200°C. Heating to 1250°C was necessary to remove the NEA from these surfaces.

Similarly, annealing hydrogen terminated diamond (110) surfaces to 800°C resulted in a positive electron affinity. But following annealing at 850°C a NEA due to deuterium was still detected. Only after annealing at 900°C could the NEA be removed from diamond (110) surfaces. Fig. 7 shows the thermal characteristics of the deuterium terminated diamond (110) surface. The results show that annealing a deuterium terminated (110) surface to 800°C causes an apparent increase in the intensity of the NEA peak while the low energy shoulder is no longer detected.

In this study, high temperature anneals were employed (up to 1250°C) to clean the diamond surfaces. It is important to ensure that none of these processes caused graphitization of the diamond surfaces. UV photoemission is very surface sensitive and could detect graphite contamination on these surfaces. Graphite shows a strong secondary peak positioned 13.5 eV below the Fermi level in UPS spectra, and a work function of 4.0 eV has

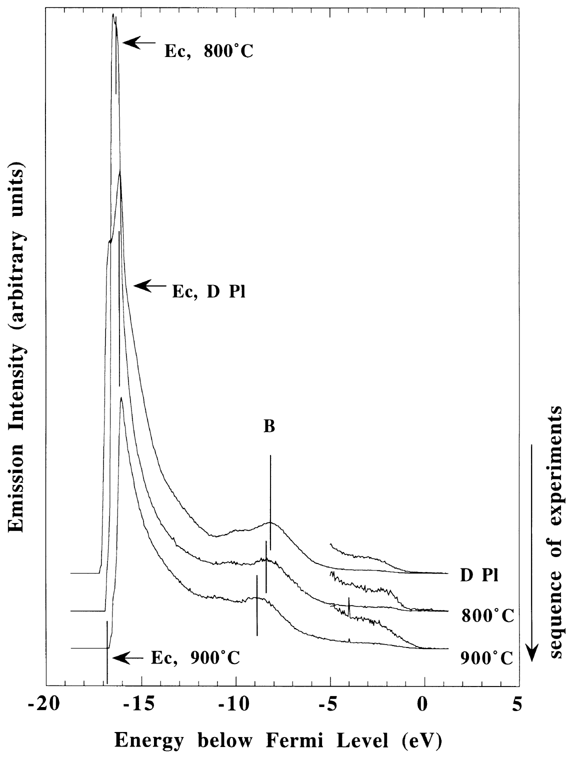


Fig. 7. UV photoemission spectra of a diamond (110) surface exposed to a deuterium plasma. The surface still exhibits a NEA following annealing at 800°C. Annealing at 900°C is necessary to remove the NEA characteristics. The sections of the spectra close to E_V and E_F have been blown up by a factor of 5.

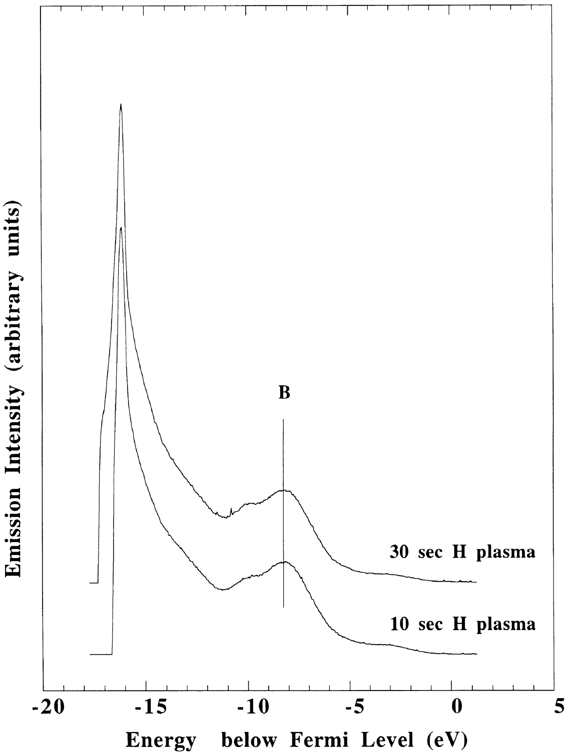


Fig. 8. UV photoemission spectra of a diamond (100) surface following two consecutive hydrogen plasma exposures. A 10 s hydrogen plasma clean results in a NEA but no emission below the conduction band minimum. After a 30 s hydrogen plasma exposure a low energy emission feature below the conduction band minimum emerges.

been measured for diamond samples that had been graphitized [24]. In the present experiments, no indication of graphitization was found in UPS spectra following neither any of the high temperature anneals nor any of the AES scans.

3.4. Low energy emission in UPS spectra

Subsequent to hydrogen or deuterium plasma treatment, several diamond (100), (111) and (110) surfaces exhibited not only a NEA peak but also an additional feature at the low energy end of UPS spectra. This feature extended to 0.2–0.4 eV below the expected position of the conduction band minimum. To examine this effect further diamond surfaces have been cleaned by H plasma exposures of different duration. For a brief (10 s) H plasma clean of diamond (100) surfaces, only a NEA peak has been observed at the low energy end (Fig. 8). The surfaces did exhibit a (2 × 1) LEED pattern, and the oxygen had been removed as determined by means of AES. For a subsequent (30 s) H plasma exposure, an additional low energy emission feature emerged. The intensity of the original NEA peak increased by ca 10%. It was also observed that with increased time of H plasma exposure, the secondary spots in the (2 × 1) LEED pattern became weaker. It may be that the H plasma leads to a breakup of the surface into domains, each exhibiting a (2 × 1) reconstruction. Note that for all of the experiments reported in this study, a gas purifier was used on the hydrogen and deuterium gas lines of the rf plasma system. Prior to the installation of this purifier it was possible to induce a NEA on diamond surfaces by means of a H plasma, but no features below the conduction band edge were observed in the UPS spectra even for extended hydrogen plasma exposures using non-purified hydrogen.

3.5. Field emission results

The field emission data typically show Fowler–Nordheim (F–N) type characteristics and can be fitted using Eq. (1) [25]:

$$I=k\left(\frac{\beta V}{d}\right)\exp\left(\frac{-6.530d\phi^{3/2}}{\beta V}\right), \tag{1}$$

where I is the current in amps, V is the bias in volts, d is the distance between the sample and the anode in microns, k is a constant, ϕ is the F–N barrier height in eV and β is the field enhancement factor. For perfectly flat surfaces and no field enhancement β is equal to 1. In this study the RMS roughness of the diamond surfaces was of the order of a few Å. It is unclear whether β would vary significantly for the observed changes in the RMS surface roughness in the Å range.

Diamond (100) and (110) surfaces were characterized by means of field emission. All data exhibited F–N type characteristics. In many instances it is advantageous to determine a threshold value for emission. The F–N expression does not extrapolate to a threshold value, however, it has become common practice to report a voltage or electric field where emission is detected. In these experiments, the emission threshold for a current of 0.1 μA will be defined. At this current the applied voltage divided by the distance (i.e. $\mathrm{V\,\mu m^{-1}}$) is termed the average field. In these experiments I–V curves were determined at a series of distances. The emission threshold current is determined at each distance and average field is calculated. Similar results were obtained at each distance. The value of the average electric field for the threshold of emission and corresponding standard deviation were deduced from the data.

For the oxygen terminated diamond (100) surface a threshold electric field of $79\pm7\ \mathrm{V\,\mu m^{-1}}$ was measured. A corresponding value of $81\pm4\ \mathrm{V\,\mu m^{-1}}$ was determined for the oxygenated C(110) surface. Field emission of the hydrogen terminated C(110) surface resulted in a lower value of $25\pm3\ \mathrm{V\,\mu m^{-1}}$ for the threshold field. These results indicate that surfaces with a positive electron affinity also have a higher threshold electric field for emission than the surfaces exhibiting a NEA.

4. Discussion

It is suggested that the appearance of a NEA on the diamond (100) surface and a (2 × 1) reconstruction is due to the removal of oxygen as discussed previously [9,26]. It is interesting to note that the intensity of the NEA peak in the UPS spectra could be increased by employing a H plasma clean. Indeed, a H plasma could also induce a NEA on a positive electron affinity surface. However, a reconstructed (2 × 1) LEED pattern could be detected after every anneal (900, 1100 and 1150°C) and H plasma exposure. Therefore the surface is thought to be terminated with a monohydride after annealing at 1050 or 900°C for the (100) surfaces cleaned by a chromic acid or an electrochemical etch, respectively. The hydrogen that terminates the surface after annealing may come from hydrogen that has diffused into the diamond. Subsequent to the removal of oxygen from the surfaces, hydrogen could bond to the vacant sites on the surface. A NEA for the monohydride terminated (2 × 1) reconstructed (100) surface has been reported before experimentally as well as based on ab initio calculations [9,11]. From these same studies a positive electron affinity was reported for the clean (2 × 1) surface. The data suggest that an adsorbate free surface could be obtained following annealing at 1100/1150°C. This means a sufficient amount of hydrogen was desorbed to remove the NEA. The feature detected at 1.2 eV below the valence band maximum following the anneals is suggested to be due to surface states. Such a feature has been observed previously at 0.95 eV below the valence band maximum [27].

A NEA peak of lower intensity was measured following the 1050°C (for samples cleaned by a chromic acid etch) or 900°C (for samples cleaned by an electrochemical etch) anneal than for a H plasma clean. After the anneals the surface is proposed to be partially terminated with a monohydride. From the intensity difference of the NEA peaks, it is estimated that about half the surface was terminated by a monohydride following the anneals. Furthermore, the remaining small low energy feature in the photoemission spectra following annealing at 1100 and 1150°C may be an indication that the hydrogen has not been removed completely from the surface. In comparison it is suggested that the H plasma results in essentially complete hydrogen surface termination.

It is notable that after electrochemical etching and a HF dip an oxygen free diamond C(100) surface can be obtained at lower annealing temperatures than for a chromic acid clean. Electrochemical etching may oxidize the diamond surfaces differently than is the case for the chromic acid process. Different configurations for oxygen bonding on diamond (100) surfaces have been proposed [10]. One configuration consists of an oxygen atom forming a double-bond with one carbon atom. Alternatively an oxygen atom could be bonded to two adjacent carbon atoms (bridge bonding configuration). The surface is (1×1) unreconstructed in either of the configurations. The surface characterization techniques available for this study were incapable of distinguishing between these two structures. Thus it was not possible to determine how the oxygen was bonded to the diamond surfaces subsequent to a chromic acid clean or electrochemical etch. Based on a surface dipole model Rutter and Robertson have calculated that the bridge bonding is expected to be more stable by 0.5 eV per surface carbon atom than the double bonding [28]. It was also observed that annealing at 500°C of chromic acid treated C(100) surfaces results in a value of +1.0 eV for the electron affinity. A value of +1.45 eV was found for annealing electrochemically etched C(100) surfaces to 500°C. Rutter and Robertson [28] have calculated a lower positive electron affinity for oxygen on C(100) in a bridge bonded configuration than in a double bonded one. The results may suggest that a chromic acid clean results in a preferentially bridge bonded oxygen termination while electrochemical etching may, on the other hand, lead to preferential double bonding of the oxygen. Independent of whether a chromic acid clean or electrochemical etching had been used, the adsorbate free (100) surfaces exhibited equivalent (within the experimental uncertainties) values for the positive electron affinity of 0.70–0.75 eV (Table 1). Further studies may be necessary to clearly understand the mechanism of the different wet chemical etching procedures, but it can be said that the electrochemical clean in combination with a HF dip apparently oxidizes the surface differently than a chromic acid etch.

The present data of the C(110) surface suggest that a reduction of electron affinity is correlated with the desorption of oxygen following annealing at 700°C, and the NEA characteristics are suggested to be due to hydrogen present at the surface. Annealing at 800°C appears to desorb a sufficient amount of hydrogen from the surface resulting in a positive electron affinity. The reports by Pate [4], Pepper [16] and McGonigal et al. [17] indicate that a large portion of the hydrogen present on the surface was desorbed between 800 and 900°C while complete hydrogen desorption was observed up to 1050°C [4]. The apparent conflict may be and indication that hydrogen could also be present in the bulk of the diamond. This may contribute to H desorption up to higher temperatures.

It should be mentioned again that it is difficult to measure the temperature of diamond due to its transparent nature [22]. The temperature values mentioned in this and other studies may be off somewhat with respect to each other. This may reconcile some of the apparent differences in the results.

In previous studies, the diamond (110) surface has always been reported to exhibit a (1×1) LEED pattern [4,12–14]. There has been considerable difficulty in producing high quality (110) diamond surfaces [15]. A (2×1) LEED pattern was observed for one (110) surface following annealing at 800°C. However, all of the other surfaces studied exhibited a (1×1) LEED pattern. In the photoemission spectra of the annealed surfaces, a feature ca 1.8 eV below the valence band edge was consistently observed. A hydrogen plasma exposure reduced this feature significantly, and this peak is attributed to surface states.

Sometimes LEED is not representative of the actual surface structure. For instance, LEED may not detect local reconstructions that can result in electronic structures observable by photoemission spectroscopy. Previous studies have reported that certain C(111) surfaces did not show reconstructed LEED patterns upon annealing [12,21], however, Himpsel et al. observed photoemission spectra indicative of a (2 × 1) reconstruction for such a sample [21]. The long range order of a reconstructed surface could be disrupted as a result of roughening or etching following process cycles such as hydrogen adsorption and desorption.

In the present experiments it was observed that oxygen could be removed at lower annealing temperatures from diamond (110) than from (100) surfaces. For all surfaces, a NEA is associated with hydrogen termination and a positive electron affinity with oxygen termination. Correspondingly a NEA could be induced at lower temperatures for the (110) surfaces than the (100) surfaces. For diamond (111) surfaces a NEA could be obtained at even lower temperatures. From the experimental evidence it can be concluded that oxygen is bonded most strongly on diamond (100) surfaces. The top layer of atoms on the unreconstructed surface are bonded with two bonds to the atoms beneath while the other two bonds are free. It has been previously reported that oxygen can be attached easily to the diamond (100) surface forming either a bridge bond between two carbon atoms or a double bond to one carbon atom [10]. On the C(111) surface the carbon atoms in the top layer are connected with three bonds to the next layer underneath. The fourth bond is oriented perpendicular to the surface. Assuming a truncated-bulk C(110) (1 × 1) surface the carbon atoms in the top layer have one bond available. Thus the (1 × 1) C(111) and (110) surfaces each have one bond available. It follows that for a C(110) surface, the temperature necessary to induce a NEA (700°C) is close to the one for the C(111) surface (600°C). [A few C(111) surfaces exhibited a NEA directly after a wet chemical clean.] However, the temperature necessary to remove oxygen from C(100) surfaces (900°C) is somewhat higher.

Our results of deuterium on C(100) are in agreement with the study by Francz et al. in that:

(1) deuterium exposure of the C(100) surface reduced the emission feature at 1.2 eV below E_v; and
(2) a NEA was observed for the deuterated C(100) surface.

Strong NEA peaks of similar high intensity were found for both hydrogen and deuterium termination.

As noted in Section 2, the value of 1250°C for the deuterium desorption temperature from a C(100) surface is somewhat higher than the value of 1177°C found by Smentkowski et al. [19]. This may be due to a difference in the temperature of the sample and holder.[22]

For C(100) and C(110) surfaces the annealing temperature necessary to remove a NEA due to deuterium was higher than for the case of hydrogen. This is attributed to an isotope effect due to the different mass of the atoms that results in a lower vibrational frequency and consequent changes in the desorption and/or diffusion kinetics of deuterium relative to hydrogen. Otherwise the NEA characteristics of hydrogen – or deuterium terminated diamond surfaces were found to be comparable. Similar effects may be expected for the C(111) surface.

The emission observed below the conduction band minimum after an extended hydrogen or deuterium plasma may be a result of band bending. The band bending may be due to states in the bandgap that cause Fermi level pinning. Another possibility is H passivation of the boron acceptors near the surface which will lead to different band bending for the different regions on the surface. In either one of these two cases the surface could consist of different domains exhibiting differences in band bending. If the spectrum is a superposition from regions with different surface Fermi levels, the spectrum will appear broader with additional features at both the valence band and the low energy cutoff. Since the spectral intensity is strongest at the low energy end, it is likely to be most evident here. Another explanation may be that emission due to excitons occurs. Bandis and Pate have described this effect for C(111) surfaces exhibiting a NEA [29]. Such an effect could lead to emission below the conduction band edge even while the band bending is constant for the entire surface. However, the exciton binding energy of

80 meV [29–31] is small compared to the observed extension of the UPS spectra below the conduction band minimum.

The field emission results suggest that diamond surfaces exhibiting a NEA has a lower threshold for field emission than those with a positive electron affinity. The field emission process is more complicated than photoemission since it includes contributions from carrier injection at the back interface, conduction through the bulk, and finally emission from the surface into vacuum. The last step may be the same for both photo- and field emission. Because of the added complexity, it is often difficult to attribute changes in the effective barrier height to specific differences in the samples. While field emission is often described by the F–N expression, it should be noted that this expression was derived for emission from metal surfaces, assuming no field inside the bulk of the material. An equation for microscopic dielectric regions has been proposed [32], but this approach would not be a reasonable model for the present case with a diamond substrate thickness of 0.25 mm.

Bandis and Pate [33] have performed simultaneous field emission and photoemission measurements from H(111)-(1 × 1) natural p-type diamond to investigate the origin of the field emitted electrons. Since this surface exhibited a NEA, the position of the conduction band minimum could be determined. The electrons due to field emission are reported to originate from near the valence band maximum.

Here p-type diamond samples were also studied. For UV photoemission spectroscopy electrons originating from the conduction band minimum can be freely emitted from a NEA surface. In comparison, electrons emitted from the valence band maximum have to overcome a barrier even for a surface with a small NEA. Calculations for hydrogen terminated diamond surfaces suggest that an electron affinity as low as -3.4 eV is obtained [11]. Inducing a NEA on a positive electron affinity diamond surface would then reduce the surface energy barrier significantly but not entirely remove it for field emitted electrons. Thus the results presented here are in agreement with the conclusions of Bandis and Pate, suggesting that field emission from p-type diamond is due to electrons in valence band states.

5. Conclusions

The replacement of oxygen with hydrogen has been found to induce a NEA on C(100), (111) and (110) surfaces. This effect was achieved by an anneal or a H plasma exposure. A high temperature anneal capable of removing the adsorbed hydrogen resulted in clean surfaces exhibiting a positive electron affinity. The present studies indicate that oxygen was bonded most strongly to the diamond (100) surface and most weakly to the diamond (111) surface. According to the annealing temperatures necessary to remove a NEA from hydrogenated diamond surfaces, the hydrogen termination on the diamond (100) surface appears to be the most stable while that of the (110) the least thermally stable. Deuterium termination of diamond surfaces was found to be stable up to higher temperatures than a corresponding hydrogen termination. This was attributed to a higher thermal desorption temperature due to the increased mass relative to H. A reduction in field emission threshold was found to be correlated with a lowering of the electron affinity. The results indicate that for p-type diamond surfaces photoemitted electrons originate from the conduction band minimum, while field emitted electrons appear to be emitted from the valence band maximum.

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