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# NEA peak of the differently terminated and oriented diamond surfaces

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## Abstract

The negative electron affinity (NEA) peak of differently terminated and oriented diamond surfaces is investigated by means of ultraviolet photoemission spectroscopy. Electron emission measurements in the range below the conduction band minimum (CBM) up to the vacuum level  $E_{\text{vac}}$  permit the quantitative calculation of the upper limit of the NEA value. The inelastic scattering at the surface to the vacuum interface and the emission of electrons from the unoccupied surface states, situated in the band gap, are the mechanisms responsible for explaining this below CBM emission. All the H-terminated diamond surfaces present NEA. However, the characteristic NEA peak observed in the spectra is only detected for the (100)-(2×1):H surface and to a lesser extent for the (110)-(1×1):H surface, while it is absent for the (111)-(1×1):H surface because of the  $k_{\parallel}$ -conservation in the photoemission process. © 1999 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Diamond; Electron emission; Hydrogen; Low index single crystal surfaces; Photoelectron spectroscopy; Surface electronic phenomena; Surface structure

## 1. Introduction

Electrons in the conduction band are generally prevented from escaping into the vacuum by the electron affinity barrier  $\chi$ . However, the diamond (100), (110) and (111) surfaces are known to exhibit a negative electron affinity (NEA) when terminated with hydrogen [1–6]. NEA is defined if the vacuum level  $E_{\text{vac}}$  lies below the conduction band minimum (CBM) at the surface and, hence,

electrons excited into the conduction band can easily escape into the vacuum. The attractive NEA property of diamond surfaces has gained a lot of interest in recent years as a result of its potential application as a low-voltage field emission device [7–10], or as a surface channel field-effect transistor [11,12]. The diamond-based devices show even better characteristics owing to a hydrogen termination, inducing a NEA behavior [13–15]. Field-emission measurements [8–10] on nitrogen-doped diamond show threshold fields less than  $0.5 \text{ V } \mu\text{m}^{-1}$ . The mechanism of emission and the corresponding link to NEA are still not well understood. Very recently, Geis et al. [16] proposed a new surface electron-emission mechanism in dia-

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mond cathodes based on the enhancement of electric fields at metal–diamond–vacuum triple junctions. They explained the mechanism as electrons tunneling from a metal into diamond surface states where they are accelerated to energies sufficient to be ejected into vacuum. For a better understanding of the emission process and its optimization for the synthesis of thin diamond films, the exact determination of the NEA peak as well as the NEA value as a function of surface termination and surface orientation are of prime importance.

In this work we present an investigation of the NEA peak as well as quantitative NEA values of the different terminated and oriented diamond surfaces. We discuss the presence of the NEA peak combined with the  $k_{||}$ -conservation in the photoemission process. We demonstrate that for differently oriented diamond surfaces, the NEA peak is present when the  $k_{||}$ -conservation in the photoemission process is satisfied. We will further show that NEA is not only limited to hydrogen termination, but also a hydrogen oxide at the surface can even result in a stronger NEA in agreement with calculations.

## 2. Experimental methods

The hydrogen plasma cleaned crystals [6,17] are mounted on a heatable (up to 1200°C) sample holder. They are transferred to a VG ESCALAB Mk II spectrometer with a base pressure of  $2 \times 10^{-11}$  mbar, equipped with a MgK $\alpha$  ( $h\nu = 1253.6$  eV) anode and a helium discharge lamp (He I,  $h\nu = 21.2$  eV). The energy resolution is at its best 0.9 eV for X-ray photoelectron spectroscopy (XPS) and 35 meV for ultraviolet photoelectron spectroscopy (UPS) with He I radiation. The diamond substrates used in this study are boron-doped, natural type IIb (B-doped,  $N_A = 10^{16}$  cm $^{-3}$ ) (100), (110) and (111) crystals. They are oriented within 3° of the crystallographic planes and the surface roughness of the as-received crystals is more than 2 nm RMS [17]. Our natural diamond surfaces were mechanically polished by Meyer AG (Anton Meyer & Co. Ltd, Biel, Switzerland) and afterwards cleaned by microwave

hydrogen plasma at 870°C at a hydrogen pressure of 40 mbar in order to smooth and to clean the surface [6,17]. After the microwave hydrogen plasma treatment, the surface roughness of the crystals is less than 10 Å RMS [6].

The surfaces present no surface contamination (less than 0.5 at.% of oxygen which is the detection limit of the technique) as shown by the MgK $\alpha$  X-ray photoelectron normal emission overview spectrum [4,18,19]. Even after several weeks exposure to air, the surfaces present no surface contamination. The so-treated hydrogen-terminated (100) surface presents a  $(2 \times 1)$  reconstruction as shown by the low energy electron diffraction (LEED) pattern [4,17] and by the atomic resolution scanning tunneling microscopy (STM) images [6,20]. The hydrogen-terminated (111) surface shows a  $(1 \times 1)$  reconstruction as shown by very high quality LEED patterns [21] and by the atomic resolution STM images [6,21]. Finally the hydrogen-terminated (110) surface has a  $(1 \times 1)$  reconstruction as shown by the LEED patterns [21].

## 3. Results and discussion

In Fig. 1 we present the low kinetic energy part of the He I normal emission spectra of the hydrogen-terminated diamond (100), (110) and (111) surfaces. The numbers in the graph present the cutoff energy position with extrapolation to zero intensity estimating an error of 0.1 eV. This error value is estimated from the error for the determination of the energy position and by the reproduction of the results (surface preparation) [6]. At low kinetic energies the hydrogen-terminated (100), (110) and (111) surfaces show a high intensity with the spectra cutoffs at 3.9, 3.9 and 4.2 eV, respectively. The cutoff energy position for the H-free surfaces is situated at higher kinetic energies around 5 eV [6,18]. The NEA-peak characterizing the electrons from the CBM, determined at 4.9 eV in the UP spectrum by extrapolation to zero intensity, is only observed for the (100)- $(2 \times 1)$ :H surface and to a lesser extent for the (110)- $(1 \times 1)$ :H surface while it is absent for the (111)- $(1 \times 1)$ :H surface. The NEA peak with its cutoff extrapolated to zero intensity corresponds,

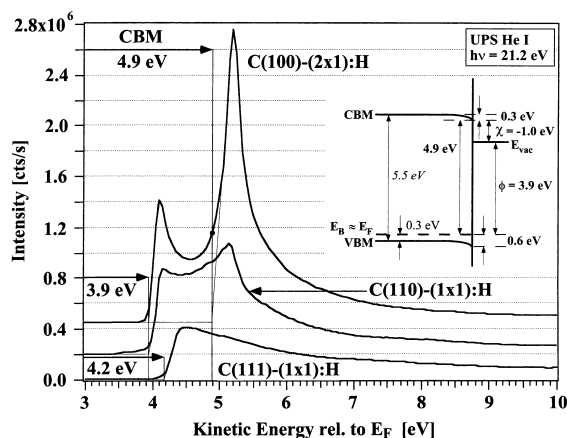


Fig. 1. Low kinetic-energy part of the He I ( $h\nu = 21.2$  eV) normal emission spectra of the H-terminated boron-doped diamond (100), (110) and (111) surfaces. The energy scale is corrected for an applied bias voltage of  $-1.5$  V to overcome the work function of the analyzer. The inset shows a energy band diagram for the boron-doped (100)-(2  $\times$  1):H diamond surface. The values are estimated to lie within an error value of 0.1 eV. The values from the literature are written in *italic style*, the calculated values in *plain style* and the measured values in **bold style**.

therefore, to the position of the CBM at the surface and will be used for the following calculations of the electron affinity value. Subtracting the energy distance from the Fermi level  $E_F$  to the CBM ( $E_F - \text{CBM} = 4.9$  eV) and the band gap (5.5 eV), we obtain 0.6 eV for the energy distance from the valence band maximum (VBM) to the Fermi level  $E_F$  (i.e.  $\text{VBM} - E_F$ ). The determined energy distance  $\text{VBM} - E_F$  is in agreement with earlier He II measurements [4]. The determination of the VBM position in the He II parts of the spectra is only correct provided that there are no occupied surface states and that states near the  $\Gamma$ -point of the bulk Brillouin zone (BZ) are probed. The diamond (100)-(2  $\times$  1):H surface is known to have no occupied surface states near  $E_F$  [18], states near the  $\Gamma$ -point of the bulk BZ are probed and, therefore, the determination of the VBM for this surface termination is possible. Calculations [6] predict the bulk Fermi level at 0.30 eV above the VBM and therefore a downward band bending of 0.3 eV can be deduced [6] as shown in the inset of Fig. 1.

The low kinetic-energy electron emission spectrum of the (100)-(2  $\times$  1):H surface shows that

below the NEA peak we measure a low kinetic-energy peak or shoulder with an abrupt cutoff situated below the CBM. This abrupt cutoff can be due to the fact that the vacuum level is situated at this position. By secondary electron-emission spectroscopy, Yater et al. [22] also observed this low kinetic energy shoulder for the caesiated diamond (100) surface. They suggested that for a strong NEA, low kinetic-energy electrons at the surface which populate energy levels below the CBM can still be emitted into the vacuum. The inelastic scattering at the surface to the vacuum interface and the transitions of electrons from the CBM to unoccupied surface states, situated in the band gap, are potential possible mechanisms [22]. The direct excitation from the valence band is another possible mechanism to populate the unoccupied surface states. A non-uniform hydrogen-terminated surface resulting in two peaks (reflecting regions with different pinning positions of the surface Fermi level) is less possible. First, you have to observe the different pinning positions of the surface Fermi level with core level photoelectron spectroscopy. Secondly, the two components of the NEA peak and of the C 1s core level have to show the same proportions. The first aspect is observed for all three orientations where a shoulder at higher binding energies is observed [18]. In effect, the second condition is only partly satisfied for the (100) surface while it fails for the (110) and (111) surfaces. Another indication is that for the (111) surface we should not measure photoelectrons at low kinetic energies in order to satisfy the conservation of the parallel wave vector component ( $k_{||}$ ) in photoemission discussed below. The NEA peak consists of low kinetic-energy electrons with diffusion lengths between 150 and 250  $\mu\text{m}$  [23] and, therefore, it contains bulk and surface contributions submitted to the  $k_{||}$ -conservation in photoemission. The low kinetic-energy peak or shoulder below the NEA peak consists only of low kinetic-energy electrons emitted from the surface (by inelastic scattering or by emission from surface states). On one side, subtracting the NEA peak, the low kinetic-energy spectrum is similar to the background resulting from secondary electrons due to the inelastic scattering at the surface to the vacuum interface. This

hypothesis fits well for the (110) and (111) surfaces and partly for the (100) surface. The intensity of the background only increases as a function of the applied bias voltage (to overcome the work function of the analyzer) due to the increased field between sample and analyzer. The photoelectron emission from the unoccupied surface states would not increase so strongly as a function of the applied bias voltage. On the other side, for the (100) surface, the low kinetic-energy peak below the NEA peak also includes photoelectron emission from unoccupied surface states. Transitions of electrons from the CBM or the direct excitation from the valence band to the unoccupied surface states, situated in the band gap, seem to be the most probable mechanisms. An indication for this is that the lowest unoccupied surface states of the (100)-(2 × 1):H surface are localized at the  $\bar{\Gamma}$  point at 1 eV below the CBM [24] exactly where we measure the sharp feature at the spectra cutoff. The occupied surface states for this surface are situated 2.3 eV below the VBM [24,25]. For the (110)-(1 × 1):H and (111)-(1 × 1):H surfaces, the unoccupied surface states at the  $\bar{\Gamma}$  point are localized at lower energies or are absent, respectively [26,27]. Using a band mapping method Jiménez et al. [28] determined the width of the valence band to be 23 eV. These measurements encourage the mechanism of direct excitation from the valence band to the unoccupied surface states using a photon energy of 21.2 eV (He I). By measuring these low kinetic-energy electrons, we are always near the  $\bar{\Gamma}$  point using the formula given in the reference [25], and therefore, we cannot measure the dispersion of these states. Using photoelectron yield spectroscopy, Ristein et al. [23] also measured photoelectrons below the CBM, but accorded them to emission from defect states. This is a clear indication that you can populate these states by direct excitation from the valence band.

Considering the low kinetic-energy cutoff as the upper value of the vacuum level (even it can lie below), we can deduce an upper value of the NEA value  $\chi$  by the distance  $\text{CBM} - E_{\text{vac}}$ . The obtained maximal NEA values for the differently oriented diamond surfaces are shown in Table 1. For the H-terminated B-doped diamond (100), (110) and

Table 1

Upper limit of the negative electron affinity (NEA) value  $\chi$  and of the work function  $\phi$  for the differently terminated and oriented diamond surfaces determined in the low kinetic-energy part of the normal emission He I spectra from Figs. 1 and 3

	NEA [eV]	$\phi$ [eV]
B-doped C(100)-(2 × 1):H	−1.0	3.9
B-doped C(111)-(1 × 1):H	−0.9	4.2
B-doped C(110)-(1 × 1):H	−1.0	3.9
B-doped C(100)-(2 × 1):OH	−1.1	3.8

(111) surfaces, the obtained maximal NEA values are −1.0, −1.0 and −0.9 eV, respectively. For the (111) surface, the band bending is only 0.1 eV and therefore we would expect the CBM at 5.1 eV [6]. These results show that the absolute NEA values show little differences in function of the surface orientation. The NEA peak itself is related to the surface orientation of the diamond crystal.

To explain the behavior of the NEA peak observed for the H-terminated diamond surfaces with different surface orientations, we show in Fig. 2 the high symmetry plane of the [011] and [100] directions of the bulk Brillouin zone. Boron-doped diamond is a semiconductor with an indirect band gap, which can affect the escape probability

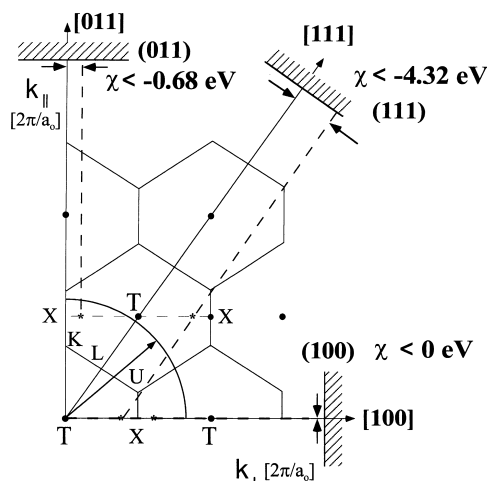


Fig. 2. High symmetry plane of the [011] and [100] directions of the bulk Brillouin zone. The minimum of the conduction band in the  $\Gamma$ X direction is shown by stairs as well as the corresponding parallel projections to the different surface normal.

of electron emission for different oriented diamond surfaces. The CBM is at  $k_{\min} = 0.76k_x$  in the [100] direction [29] where  $k_x$  is the zone boundary wavevector. For the (100) surface electrons from the CBM arrive with a zero  $k_{\parallel}$  while for the (111) surface CBM electrons arrive with a large  $k_{\parallel}$  (Fig. 2). Kane et al. [30,31] established a one-electron escape model of electron emission from a perfect surface and required in this model not only the conservation of energy, but also the conservation of  $k_{\parallel}$ . In addition,  $k_{\parallel}$ -conservation of NEA surfaces acts in some cases as a barrier to low kinetic-energy electrons with large  $k_{\parallel}$ . Bandis et al. [32] have analyzed this constraint for the diamond (111) surface and found that  $\chi$  must be less than  $-4.55$  eV in order to satisfy the energy and  $k_{\parallel}$ -conservation. However, for the (111) surface,  $\chi$  is above  $-4.55$  eV, and therefore the electrons are totally internally reflected at the diamond–vacuum interface. We have calculated this constraint for the (111) and (110) surfaces and found that  $\chi$  must be less than  $-4.32$  eV and less than  $-0.68$  eV, respectively, in order to satisfy the energy and  $k_{\parallel}$ -conservation in photoemission. Indeed, for the (110)-(1×1):H surface,  $\chi$  is less than  $-0.68$  eV and therefore we observe a weak NEA peak. But the conditions, in order to satisfy the energy and  $k_{\parallel}$ -conservation, are not favorable compared with those for the (100) surface. This explains the fact that the NEA peak of the (110)-(1×1):H surface is not as high as for the (100)-(2×1):H surface.

The NEA values ( $-1.0$  and  $-0.9$  eV) for the (100) and (111) surfaces are slightly larger than those measured by Bandis and Pate [2,33] ( $-0.8$  and  $-0.7$  eV). These different NEA values could arise from the fact that the crystals, as well as the surface preparation methods, were not always the same. For the (100) surface, the electron affinity change of  $2.3$  eV [6] is similar to the one observed by Thomas et al. [34] ( $2.2$  eV) and to the one calculated by Rutter et al. [35] ( $2.54$  eV). But it differs from the value observed by Cui et al. [36] ( $1.65$  eV) and to the one calculated by Zhang et al. [37] ( $3.0$  eV) who found a NEA value of  $-2.2$  eV.

The low kinetic-energy part of the He I ( $h\nu = 21.2$  eV) normal emission spectra for the H- and OH-terminated diamond (100) surfaces are shown

in Fig. 3. The OH-terminated (100) surface was obtained by a hydrogen/oxygen plasma and the surface shows the same ( $2 \times 1$ ) reconstruction as for the H-terminated surface. The oxygen coverage was checked by core level photoemission. The maximal NEA value for the OH-terminated (100) surface is  $-1.1$  eV,  $0.1$  eV higher than for the H-terminated surface. A similar phenomenon is known for the Cs–O-terminated diamond surface [38]. A surface with different regions that are partially O- and H-terminated would show a lower NEA peak and the spectra cutoff at higher kinetic energies than for the fully hydrogen-terminated surface. Generally we have done the plasma treatments for more than 1 h, always resulting in uniform terminated surfaces [17]. Agreement between our measurements and the calculations by Rutter and Robertson [35] is not found for the absolute NEA values, but is found for the electron affinity change between the H-saturated and H-free termination as well as for the electron affinity difference between H- and OH-termination. For the H- and OH-terminated (100) surfaces, the calculated values are  $-2.05$  and  $-2.13$  eV [35], while the measurements from Fig. 3 reveal NEA values of  $-1.0$  and  $-1.1$  eV, respectively. The absolute NEA values do not agree, but the difference in the NEA value ( $0.08$  eV) shows agreement between

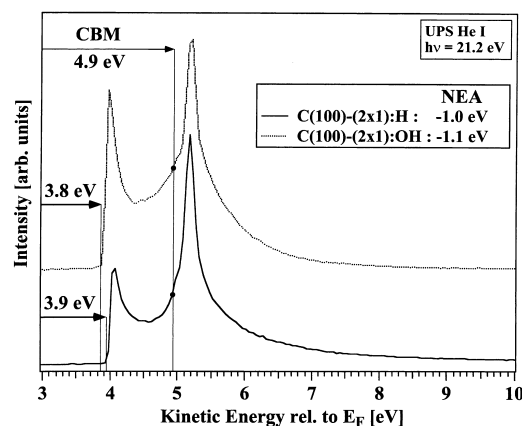


Fig. 3. Low kinetic-energy part of the He I ( $h\nu = 21.2$  eV) normal emission spectra of the H- and OH-terminated boron-doped diamond (100) surfaces. The energy scale is corrected for an applied bias voltage of  $-1.5$  V to overcome the work function of the analyzer.



our measurements and the calculations. The larger NEA value for the OH-terminated (100) surface is due to the OH bond that produces a dipole opposing the CO bond and therefore enhancing the NEA more than a simple CH bond [35]. The presence of NEA as a result of a surface dipole layer has been proven in detail by a recent analysis of the electron affinity [36] as well as by a theoretical study [35].

#### 4. Conclusions

In summary, the NEA peak of differently terminated and oriented diamond surfaces was investigated by means of ultraviolet photoelectron spectroscopy. Electron emission from energy levels below the CBM up to the vacuum level  $E_{\text{vac}}$  allowed the quantitative calculation of the upper limit of the NEA value. The inelastic scattering at the surface to the vacuum interface and the emission of electrons from the unoccupied surface states, situated in the band gap, are the mechanisms responsible for explaining this below CBM emission. All the H-terminated surfaces present NEA with an upper limit of  $-1.0$  eV for the boron-doped diamond crystals. The characteristic NEA peak of the ultraviolet photoelectron spectrum is only observed for the (100)-(2×1):H surface and to a lesser extent for the (110)-(1×1):H surface while it is absent for the (111)-(1×1):H surface because of the  $k_{\parallel}$ -conservation in the photoemission process.

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