Electron Affinity of the Bare and Hydrogen Covered Single Crystal Diamond (111) Surface

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The electron affinity χ and the band diagram of single crystal diamond (111) surfaces was determined as a function of hydrogen coverage by combining work function measurements with photoelectron yield and core level photoemission spectroscopy. χ ranges from -1.27 eV for the fully hydrogen covered (1×1) surface to $+0.38$ eV for the hydrogen free (2×1) reconstructed surface. This change is quantitatively explained by a surface dipole model provided a coverage dependent depolarization is included. The dipole moment of the C-H bond on diamond (111) is found to be 0.09 eÅ. [S0031-9007(98)06605-8]

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Among the outstanding traits of diamond ranks a property that it shares with no other semiconductor: a highly stable intrinsic negative electron affinity (NEA). When in a semiconductor an electron is raised from the valence band to the conduction band minimum (CBM) by light, for example, such an electron is not free to leave the sample because at the surface it encounters an energetic barrier of a few eV, the electron affinity χ. The crystal has a positive electron affinity (PEA). From a diamond single crystal surface coming from the polisher's wheel or synthesized by chemical vapor deposition (CVD), however, an electron at the CBM is free to leave the crystal because such a barrier does not exist; χ is negative and consequently the surface has negative electron affinity (NEA). The negative electron affinity of diamond is stable in air up to several hundred °C and its most conspicuous consequence is a yield of photoelectrons that exceeds that of a surface with PEA by several orders of magnitude [1,2]. Diamond with NEA surfaces has a considerable potential for highly efficient solar blind photocathodes and for cold cathode emitters to be used in flat panel devices [3]. For a microscopic understanding of the emission process and its optimization, an exact value for $\chi < 0$ as a function of surface condition is of prime importance.

There appears to be a general consensus that NEA has something to do with the hydrogen termination of the diamond surface. For example, the phase transition from an unreconstructed diamond (111) surface to a (2×1) reconstructed surface at about 900–1000 °C that is due to the loss of hydrogen is also accompanied by a transition from NEA to PEA [4,5]. The fact that a diamond surface exhibits NEA is readily detected by comparing the threshold of photoelectron emission with the band gap [5–7]. However, to determine a value of $\chi < 0$ is in principle not possible by these techniques.

In this Letter we present measurements of χ for diamond (111) surfaces when they are in the state of NEA and of PEA. We demonstrate that the evolution of χ follows the coverage of the surface with hydrogen and show that the total change in χ from its maximum value to its minimum is quantitatively explained with the formation of a dipole layer at the diamond surface provided depolarization effects are properly taken into account. The dipoles are due to a charge transfer between the H adatoms and the topmost layer of C atoms with a dipole moment that follows from simple electronegativity arguments. In order to determine χ as a function of hydrogen coverage, hydrogen was desorbed from a fully hydrogenated diamond (111)-(1×1):H surface by isothermal annealing at 1000 K through the (1×1) to (2×1) surface phase transition under ultrahigh vacuum (UHV) conditions ($p = 10^{-8}$ Pa).

The sample used in this study was a natural type IIb diamond (111) single crystal with dimensions of $3 \times 5 \times 0.3$ mm^3, a boron concentration of about 10^{16} cm^{-3} as determined by infrared spectroscopy, and a conductivity of the order of 1 Ω^{-1} cm^{-1}. From the boron concentration and the energy of the acceptor level (0.36 eV), the Fermi level position in the bulk is calculated to lie 0.32 ± 0.01 eV above the valence band maximum (VBM) using reasonable limits for the compensation ratio of 0 to 0.2. The as-received diamond surface had been mechanically and hydrogen plasma polished which produces an atomically flat surface [8,9]. After an anneal under UHV conditions at 1400 K for 12 min to desorb surface contaminations, it was treated in a hydrogen plasma at about 1100 K for 10 min to provide a controlled surface hydrogenation. The so treated diamond surface showed a sharp 1×1 low energy electron diffraction (LEED) pattern, and the prominence of strong dispersion in the angle resolved photoemission spectra indicated a complete ordering of the surface [10]. There was no trace of oxygen or other contaminants on the as-hydrogenated diamond surface as evidenced by x-ray induced photoelectron spectroscopy (XPS). The diamond sample clamped on a Ta foil was heated by electron beam bombardment from the back. The temperature of the diamond sample was measured by a newly developed method which employs the Raman line position of diamond as a measure of temperature [11]. In this way the temperature of diamond itself

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and not that of the sample holder is accurately determined to within ±10 K.

The electron affinity χ is defined as the energy difference between the vacuum level E_{vac} and the conduction band minimum E_c. With reference to Fig. 1, this quantity can be expressed in terms of the work function ϕ, the Fermi level E_F, the top of the valence band E_V, and the energy gap E_g (5.47 eV at room temperature) as

$$\chi = E_{\mathrm{vac}} - E_C = \phi + (E_F - E_V) - E_g . \quad (1)$$

Because the top of the valence band is difficult to determine for diamond, we determined the change in electron affinity $\Delta\chi$ by measuring the change in work function $\Delta\phi$ and that in $(E_F - E_V)$ simultaneously as a function of annealing time. These changes are referred to an absolute scale by monitoring the point where χ changes sign via photoelectron yield spectroscopy.

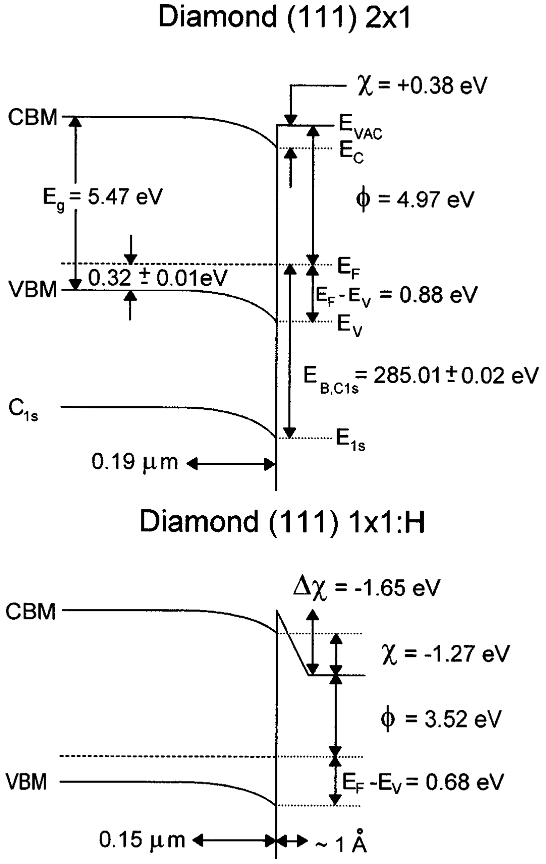

FIG. 1. Band diagram of a type-IIb single crystal diamond at the (111) surface. The energies given are the result of the analysis in the text. Upper panel: Clean (2 × 1) reconstructed diamond (111) surface with positive electron affinity. Lower panel: Hydrogen saturated, unreconstructed diamond (111) surface with negative electron affinity. Note the different width of the surface depletion layer (~0.15 μm) and the surface dipole layer (~1 Å). The error given for $C1s$ binding energy represents the experimental uncertainty and the one given for the bulk Fermi level position results from the unknown number of compensating donors in the material. The absolute scale for all other energies quoted is based on the crossover from NEA to PEA with an uncertainty of ±0.065 eV.

The work function of diamond was measured through the contact potential difference (CPD) relative to a gold coated reference surface of known work function using the Kelvin method [12]. The CPD is equal to $\Delta\phi$ and can be measured with an accuracy of ±10 meV. This method works for metals and for semiconductors independent of the sign of the electron affinity and the presence of surface states as long as the sample is sufficiently conductive. The latter condition is fulfilled for our sample. Changes in $E_F - E_V$ are in general changes in surface band bending that occur in the course of the hydrogen desorption. They were measured by following the binding energy of the $C1s$ core level relative to E_F using monochromatized XPS with a resolution of 0.5 eV. Because the $C1s$ level has a fixed energy separation from the valence band maximum, these measurements yield $\Delta(E_F - E_V)$ to within ±0.05 eV. Note, that the surface band bending extends over a distance (150 nm) large compared to the probe depth (2 nm) of photoemission. The photoelectron yield measurements, finally, were performed with the same high sensitive setup that was used earlier by us in work on diamond surfaces with NEA [2].

The experiment proceeds as follows: After hydrogenation the work function ϕ and the $C1s$ binding energy $E_B(C1s)$ are measured. Then the sample is taken in a few steps up to 1000 K. At this temperature the sample is kept for a finite amount of time, then cooled down to room temperature, and ϕ, $E_B(C1s)$, and the yield spectrum are measured and the reconstruction of the surface is monitored by LEED. Repeating these steps 11 times and annealing the sample thus for a total of 12 000 s at 1000 K, the hydrogen is desorbed and the surface goes from a (1 × 1) surface with NEA to a (2 × 1) reconstructed one with PEA. In Fig. 2, we have plotted the variation in χ as a function of annealing time. The data points are derived from the CPD measurements and encompass the correction for changes in band bending. The initial value of χ indicated by the horizontal bar in Fig. 2 corresponds to the nonannealed state and the data points (full squares) to the isothermal annealing sequence afterwards. Between the as-prepared state and the start of this sequence, the sample had already been annealed for a total of 28 min at various temperatures <1000 K, resulting in a change in χ of +0.50 eV. To include this change into the isothermal annealing sequence requires to place it in advance of the second data point by an effective time t_{eff} that would cause the 0.5 eV change in χ in a single annealing step at 1000 K. Because t_{eff} depends on the kinetics of the process responsible for changes in χ, we have just indicated upper (28 min) and lower (0 min) limits for t_{eff} by the length of the bar.

The changes in χ which are directly measured are converted to absolute χ values by monitoring the transition from NEA to PEA using yield spectroscopy. Figure 3

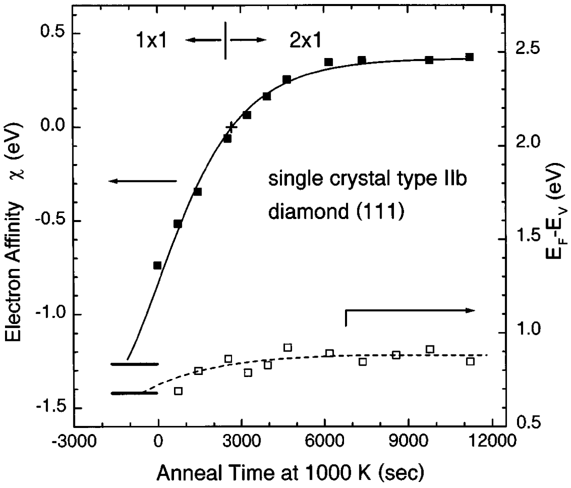

FIG. 2. The electron affinity χ (solid squares) and the Fermi level position relative to the valence band maximum (open squares) as a function of annealing time at 1000 K. The solid line through the data points for χ is the result of a fit to Eq. (2) assuming first order desorption kinetics of hydrogen. The dashed line is a guide to the eye. The cross marks the transition from NEA to PEA.

shows yield spectra taken for the as-hydrogenated sample and after 42 and 54 min of anneal time, respectively. The first two spectra are characteristic for surfaces with NEA because the photoelectron yield rises sharply when the photon energy reaches the band gap of diamond at 5.47 eV. This can be taken as a reliable fingerprint for NEA as discussed by Bandis *et al.* [13] and by Ristein *et al.* [2]. After 54 min annealing time this fingerprint is absent because the vacuum level is now above E_C. We thus place the point corresponding to $\chi = 0$ in the middle between the 42 and 54 min anneal (cross in Fig. 2). In this way χ is referred to an absolute scale with an accuracy of ±0.065 eV because the change in χ amounts to 0.13 eV between 42 and 54 min annealing time.

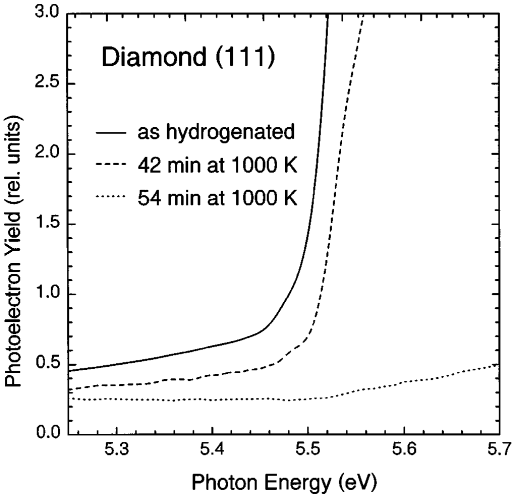

FIG. 3. Total photoelectron yield spectra of a single crystal diamond (111) recorded for the as-prepared surface and at the transition from NEA and PEA. The sharp increase in electron emission (solid and dashed lines) for photon energies equal to the band gap is the signature of NEA.

The change in Fermi level relative to the top of valence band (open squares in Fig. 2) was monitored by the $C1s$ binding energy as described above, and this change was referred to an absolute value through Eq. (1) using the saturated values of the work function ($\phi = 4.97$ eV) and the electron affinity ($\chi = 0.38$ eV). The Fermi level lies 0.68 eV above the surface VBM for hydrogen terminated and 0.88 eV for H-free diamond (111) surfaces. This is equivalent to a downward band bending that increases from 0.36 to 0.56 eV (compare Fig. 1).

The saturation value of χ for the dehydrogenated surface is thus measured to be $\chi_{\max} = 0.38 \pm 0.07$ eV. The minimum electron affinity measured amounts to $\chi_{\min} = -1.27 \pm 0.07$ eV. This is to our knowledge the first time that this experimental quantity has been published for diamond (111) or any other surface of diamond. Bandis *et al.* [13] reported $\chi_{\max} = 0.5$ eV for the clean (111) surface and Diederich *et al.* [14] measured the same value for the H-free (100) surface. Zhang *et al.* [15] calculated electron affinities of 0.8 eV for H free and -2.2 eV for hydrogen terminated diamond (100) surfaces which are in magnitude considerably larger than the experimental values measured here.

It is our contention that the NEA is due to a surface dipole layer set up by the partially ionic C^--H^+ bond. Such a dipole layer causes a potential step ΔV perpendicular to the surface over a distance of the order of the C-H bond length of 1.1 Å. The potential step in turn implies that the vacuum level is lowered relative to E_C by $e\Delta V$ compared to its value without the dipole layer where e is the elementary charge. The reduction in χ from $\chi_{\max}$ is thus equal to $-e\Delta V$, which in turn depends on the areal density n and the magnitude p of the dipoles:

$$\chi - \chi_{\max} = -e\Delta V = -\frac{epn}{\varepsilon_0} f(n), \tag{2}$$

where ε_0 is the dielectric constant of free space. The function f which depends on n takes the interaction of dipoles into account with the result that the contribution of each dipole to ΔV is reduced for high dipole densities. An expression for $f(n)$ with the polarizability α of the dipoles as a parameter can be obtained according to the calculation of Topping [16]:

$$f(n) = \left(1 + \frac{9\alpha n^{3/2}}{4\pi\varepsilon_0}\right)^{-1}. \tag{3}$$

Considering first order desorption kinetics of hydrogen from the diamond surface, the dipole density as a function of isothermal annealing time t is given by

$$n(t) = n_0 e^{-t/\tau}, \tag{4}$$

where n_0 is the areal density of H atoms at the start of the annealing and equals thus the surface density of C atoms of 1.81×10^{15} cm^{-2} for the (111) surface. Combining Eqs. (2), (3), and (4), the change $\Delta\chi(t)$ can be calculated using τ and p as free parameters. The best fit result shown as a solid line in Fig. 2 is obtained for $\tau = 1850$ s and $p = 1.45 \times 10^{-30}$ A s m (0.09 eÅ) using a polarizability α for the C-H dipoles of 1.28×10^{-40} A s m^2/V [17]. This value was obtained from the refractive index of polyethylene which equals 1.5 using the Clausius-Mossotti relation. It should be pointed out that a satisfactory fit of the experimental $\Delta\chi(t)$ values to Eq. (2) is not possible without taking the depolarization into account. In the point charge approximation the dipole moment p is given by $p = d\Delta q$ where d is the C-H bond length and Δq the charge transfer from the more electronegative C to the H atom. Estimating Δq on the basis of the Pauling electronegativities for C (2.55) and H (2.2), we obtain $\Delta q = 0.07e$ [18]. Combining this value with the C-H bond length of 1.1 Å [19] yields $p = 1.23 \times 10^{-30}$ A s m (0.08e Å). This value is in excellent if possibly somewhat fortuitous agreement with the dipole moment arrived at from our analysis of the electron affinity.

In summary, the value of the electron affinity has been determined on NEA as well as PEA diamond surfaces by combining measurements of the work function with photoemission and total photoelectron yield spectroscopy. The band diagram resulting from these measurements for the two extreme cases is shown in Fig. 1. The change from a PEA to a NEA surface by hydrogenation is caused by a potential drop ΔV associated with a surface dipole layer consisting of polar C-H bonds. The short atomic distance over which the potential drops allows electrons to tunnel readily through the ensuing potential barrier. The considerable change in χ (1.65 eV) is mainly due to the high density of surface dipoles on account of the small lattice constant of diamond. The idiosyncrasy of the relative electronegativities of C and H with C more electronegative than H together with the large band gap of diamond combine to lower E_{vac} below E_c by hydrogenation. On Si and Ge the situation is just the opposite [18].

Finally, as a result of the 0.56 eV downward surface band bending on p-type diamond in conjunction with the inherently small positive electron affinity the condition of so called *effective* negative electron affinity is met for the bare (111) surface. This means that the *bulk* CBM lies above the vacuum level [13]. However, this effective NEA does not lead to a significantly enhanced electron emission because conduction electrons are unlikely to cross the rather wide depletion layer by ballistic transport.

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