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Surface doping: a special feature of diamond

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Abstract

A unique feature of diamond surfaces is a highly conductive p-type layer, which is usually observed when the surfaces are hydrogen terminated. This phenomenon has recently attracted a lot of interest since a number of electronic applications proposed for diamond are based on the effect. Nevertheless, its microscopic origin is still a matter of debate. In this paper we propose an electron transfer from the diamond valence band to adsorbates at the surface to be the effective doping mechanism. These adsorbates act not as isolated species but as components of a mildly acidic aqueous surface layer and thus charge exchange has to be described by electrochemical arguments. The model is supported by experiments, which show that the hydrogenation of the surface is necessary but not sufficient for inducing the hole accumulation layer at the surface.

1. Introduction

Although the band gap of diamond should render the intrinsic material a perfect insulator, Landstrass and Ravi observed more than a decade ago that nominally undoped diamond exhibits a high conductance that degrades gradually upon annealing in vacuum [1, 2]. After this phenomenon had for a long time been considered as destructive for any kind of electronic application of diamond, and consequently removed by surface oxidation prior to any device preparation, Kawarada showed surprisingly that the surface conductive layer could not only be tolerated but even exploited for efficient surface field effect devices [3]. This has inspired new interest in the phenomenon of surface conductivity and subsequent investigations led to the following picture. The value of the two-dimensional conductivity is usually of the order of 10^{-6} to $10^{-4} \Omega^{-1}$ resulting from p-type carriers with a lateral concentration in the range of 10^{12} to 10^{13} cm^{-2} and with a mobility between 10 and $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Both mobility and carrier concentration are only weakly temperature dependent [4]. These mobilities are not too different from those measured for B-doped diamond and there is thus general agreement that the carriers are holes residing in an accumulation layer at the surface [5]. The depth distribution of the acceptors responsible for the hole accumulation is discussed controversially, ranging from species at the surface [5, 6] to layers extending up to 10 nm into the diamond [4]. It has

even been suggested that the acceptors form a layer buried 30 nm below the surface [7]. In the limit of a quasi-two-dimensional acceptor layer at or closely below the surface the observed areal density above 10^{12} cm^{-2} holes requires a band profile such that the surface Fermi level lies within a few kT at the valence band maximum (VBM) (see section 3).

The surface conductivity is only observed on hydrogenated diamond surfaces and disappears after dehydrogenation or oxidation of the surface. Thus it has been suggested that hydrogen is directly responsible for the hole accumulation layer by forming particular but as yet unspecified point defects within the diamond lattice that act as shallow acceptors [4]. Based on conductivity measurements and photoelectron yield spectra we will demonstrate in the following that hydrogenation is necessary but not sufficient for the surface conductivity, and that additional species from the atmosphere are required. We shall propose a transfer doping mechanism based on an electron transfer between the diamond valence band and an electrolytic wetting layer on top of the surface, which induces the holes responsible for the surface conductivity.

2. Experimental results

We have investigated a large variety of diamond samples of different types to specify possible influences of the crystallographic surface character ((100 and (111) single crystal and mixed polycrystalline surfaces) and the impurity concentration of the bulk material below the surface. Figure 1 shows a review of the results. Two regimes of conductances can be distinguished clearly. Independent of the type of diamond the surfaces show directly after plasma hydrogenation or after CVD growth in conventional methane/hydrogen mixtures a high conductance in the microsiemens range (10^{-6} to 10^{-4} S). Also, both common deposition techniques, i.e. microwave (MW) and hot filament (HF) assisted CVD, induce surface conductivity, which rules out that ion bombardment or subplantation of energetic protons below the surface, as sometimes suspected to be a consequence of the plasma self-bias, are responsible for the phenomenon. When the diamond surfaces are treated by oxidizing acids or annealed in air (≥ 500 K) or in UHV (≥ 1000 K) the surface conductivity is lost and the conductance is in the picosiemens range (10^{-12} to 10^{-10} S). The phenomenon of surface conductivity is thus observed on all kinds of diamond and appears to depend only on the surface treatment. So far the data of figure 1 seem to indicate the equivalence of hydrogen termination and high surface conductivity. By focusing on one special experiment on a homoepitaxial CVD layer on a type Ib(100) substrate (shaded background in the middle of figure 1) we have examined this apparent equivalence somewhat more closely. In this experiment the homoepitaxial (100) diamond layer was introduced in the as-prepared state into UHV. A high conductance of 10^{-4} S was confirmed *in situ* and the hydrogenation was established by the fingerprint of negative electron affinity (NEA) of the surface as seen in the total photoelectron yield spectrum [8, 9]. This characteristic is based on the correlation between the sign of the electron affinity and the hydrogenation of the surface. When hydrogen atoms terminate the surface dangling bonds the covalent but polar C–H bonds establish an additional dipole density on top of the surface as compared to the clean surface, which lowers the electron affinity from +0.4 to -1.3 eV [10]. As a consequence, the vacuum level is at lower energy than the conduction band minimum (CBM) and conduction band electrons can escape into vacuum without any energy barrier. In that case the photoelectron quantum efficiency measured in a photoyield experiment as a function of photon energy rises steeply with a threshold exactly at the band gap energy. When the hydrogen termination of the surface is lost the electron affinity turns positive and the photoyield spectrum is completely structureless around the band gap energy (compare also figure 2 below).

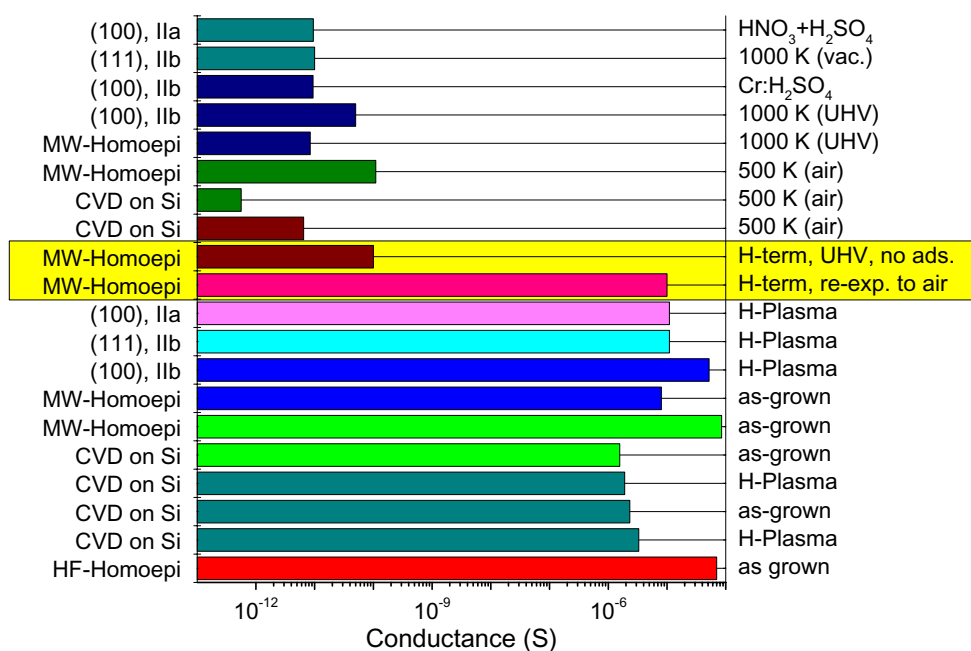


Figure 1. Surface conductance of a variety of diamond samples after different types of surface treatment. The data on the shaded background refer to a homoepitaxial diamond layer on a type Ib(100) substrate used for the UHV experiment illustrated in figure 2.

After annealing the sample in UHV at 410 °C for 15 min the conductance dropped to 10⁻¹⁰ S, while the hydrogenation remained intact as demonstrated by the NEA property of the surface. In fact, thermal desorption of chemisorbed hydrogen does not commence below 700 °C [11, 12]. We then masked half of the sample and removed hydrogen from the other half by electron beam induced desorption (1 keV, 0.2 mA cm⁻², 90 minutes). As demonstrated previously [13] this is—unlike thermal desorption—a method to remove hydrogen without introducing in addition electrically active defects. After this treatment the mask was removed *in situ* and the conductance and photoyield spectra were measured on both parts of the surface. The yield spectra are shown in the inset of figure 2. The masked area still shows the fingerprint of NEA, namely a steeply rising electron yield at the band gap energy E_g . Even the oscillatory fine structure with the optical phonon frequency of 162 meV as the period can clearly be identified, which was already found in the yield spectra of NEA single crystal diamond(111) surfaces by Bandis and Pate [8, 14]. The oscillations were analysed by the authors in terms of the thermalization dynamics and break-up of photoexcited excitons. The spectrum in figure 2 shows the same mechanism to be active also on our homo-epitaxial (100) surface and proves thus the high quality of the CVD layer. In contrast, the fingerprint of NEA is absent on the irradiated surface proving that the hydrogen termination has been removed and the electron affinity has turned positive on that part of the sample.

As also demonstrated in figure 2 both halves of the surface were in the low conductance state after annealing and remained so as long as they were kept in UHV. However, when they were brought up to the air the conductance of the masked and thus hydrogenated area rose by four orders of magnitude within the first 20 minutes of exposure and increased more slowly thereafter until it reached 10⁻⁴ S after 3 days. (In the bar graph diagram of in figure 1 the

apparent saturation value of 10^{-5} S reached after 11 000 s is listed for this experiment.) By contrast, the dehydrogenated part of the sample remained in its low conductance state with no sign of change whatsoever. This experiment clearly demonstrates that the hydrogenation of diamond is a necessary but not a sufficient condition for high surface conductivity. An additional ingredient that is obviously coming from the air and that had thermally been desorbed in UHV above 400°C is necessary as well. This conclusion is supported also by experiments of Szameitat *et al* [15] and of Koslowski *et al* [16], who both observed a recovery of the surface conductivity of polycrystalline and homo-epitaxial single crystal diamond films after it had been removed by thermal annealing in vacuum.

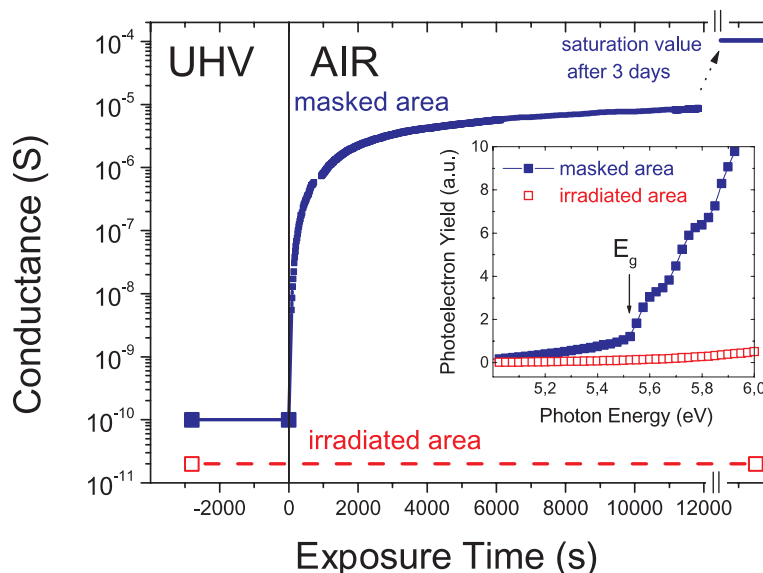


Figure 2. Conductivity transients of a homoepitaxial diamond(100) surface during re-exposure to air after the sample has been mildly annealed at 410°C in UHV and one half of it additionally dehydrogenated by electron bombardment. The Inset shows the total photoelectron yield spectra taken on both parts of the surface prior to air exposure.

3. Discussion

The UHV experiments discussed above prove that besides the hydrogen termination of the surface dangling bonds species from the atmosphere on the hydrogen terminated diamond surface are required to induce the surface accumulation. To do this they must obviously provide electronic states in the gap of diamond that can localize valence band electrons very much like conventional acceptors in bulk semiconductors do. In contrast to bulk doping such a surface doping mechanism is, however, connected with charge separation, which induces a band bending potential $W(x)$. When this potential is defined as the local energy separation between the valence band maximum E_V and the Fermi level E_F relative to the same value that is asymptotically reached in the bulk of the diamond, $W(x) = (E_V - E_F)(x) - (E_V - E_F)(\infty)$, it is related to the space charge density by $\rho(x)$ by

$$\rho(W(x)) = 2en_i \sinh(W(x)/(kT)) \quad (1)$$

where $n_i = \sqrt{N_C N_V} \exp(-E_g/(2kT))$ is the intrinsic carrier density of the semiconductor related to the effective densities of states N_C of the conduction and N_V of the valence band and the band gap energy E_g . e is the elementary charge and kT the thermal energy. Note that the space charge density does not depend explicitly but only implicitly on the depth x below the surface. Solving Poisson's equation on the basis of (1) yields an equation between the (depth integrated) total lateral charge density σ_{accu} in the accumulation layer and the surface band bending potential $W_0 = W(x = 0)$:

$$\sigma_{accu} = \sqrt{8kT\epsilon\epsilon_0 n_i} \sinh(W_0/(2kT)). \quad (2)$$

By inserting the position $[(E_C + E_V) + kT \ln(N_V/N_C)]/2$ of the intrinsic bulk Fermi level, and using $W_0 \gg kT$ to approximate the hyperbolic function in (2) by an exponential, the total charge density in the hole accumulation layer can be expressed more conveniently by

$$\sigma_{accu} = \sqrt{2kT\epsilon\epsilon_0 N_V} \exp((E_V - E_F)_{surface}/(2kT)). \quad (2')$$

Using $N_V = 2.7 \times 10^{19} \text{ cm}^{-3}$ for the effective valence band density of states [17] yields for room temperature $2.1 \times 10^{12} e \text{ cm}^{-2}$ for the pre-factor in equation (2'). This charge is just the charge density carried by the holes in the accumulation layer. In order to be compatible with the experimental value of the order of 10^{12} to $10^{13} e \text{ cm}^{-2}$ [4, 6] equation (2') requires that the exponential is of the order of unity and thus the valence band maximum (VBM) has to be bent up so much that it reaches the Fermi level at the surface. In fact, when freshly hydrogenated samples are measured by x-ray excited photoelectron spectroscopy we can find Fermi level positions from the C1s binding energy that coincide with the VBM within our experimental error. Thermal equilibrium in such a situation requires thus electronic states of the surface adsorbates below the VBM which had originally been empty and were filled by electron transfer from the diamond. Thus the electron affinity of the adsorbate has to be higher than the ionization energy $I_{C:H} = E_g + \chi_{C:H}$ of the hydrogen terminated diamond surface. Using the electron affinity $\chi = -1.27 \text{ eV}$ of hydrogenated diamond as experimentally determined by Cui *et al* [10] yields $I_{C:H} = 5.47 \text{ eV} + \chi_{C:H} = 4.20 \text{ eV}$. Electron affinities of molecular atmospheric species lie below 2.5 eV and even the most electronegative radicals, i.e. halogen atoms, do not exceed 3.7 eV [18]. Thus, direct electron transfer from the diamond into an atmospheric adsorbate appears to be impossible. It requires indeed a somewhat more complex, but very common electronic system at the surface to supply such low-lying electronic states.

Consider a thin water layer as forms naturally on all surfaces exposed to atmosphere. Such an aqueous layer in contact with atmospheric CO_2 forms a mildly acidic electrolyte with a pH value around 6 [19]. This electrolyte at the diamond surface can also exchange electrons with the diamond. The charge exchange is accompanied by a chemical equilibrium reaction between the oxonium ions and hydrogen dissolved in the electrolyte: $2\text{H}_3\text{O}^+ + 2e^- \leftrightarrow \text{H}_2 + 2\text{H}_2\text{O}$. A semiconductor like diamond brought into contact with such an electrolyte will in general inject electrons or holes and drive the equilibrium reaction at the surface into one or the other direction. In which direction electron transfer takes place will depend on the difference in chemical potentials of the semiconductor and of the electrolyte. The latter reflects the dynamic equilibrium between oxonium and hydrogen and thus depends on the concentration of the reactants and the order of the reaction via Nernst's equation

$$\mu_e = \mu_{SHE} - kT/2 \ln \left[\frac{([\text{H}_3\text{O}^+]/[\text{H}_3\text{O}^+]_{SHE})^2}{[\text{H}_2]/[\text{H}_2]_{SHE}} \right]. \quad (3)$$

As usual the density of the third reactant, water, is assumed to be constant under all circumstances and thus omitted. (For the form presented above the various reaction rates

have to be strictly proportional to the concentrations to the power of their reaction order. Deviations from this idealized situation are usually taken into account by replacing formally the concentrations by so called activities. We shall not discuss this rather formal aspect here.) Nernst's equation gives just the change of the chemical potential for the electrons as a function of the pH value and the dissolved hydrogen concentration relative to some standard conditions. These standard conditions can, for example, be chosen as those of the standard hydrogen electrode SHE (with $\text{pH} = 0$ and a saturated H_2 concentration corresponding to 1 bar of H_2 partial pressure). Then μ_{SHE} is the chemical potential of the SHE relative to the vacuum level and is given by $\mu_{SHE} = -4.44 \text{ eV}$ [20]. Following the Henry–Dalton law [21] the concentration of dissolved hydrogen can be taken proportional to its partial pressure p_{H_2} within the atmosphere and thus the ratio of concentrations can be replaced by the ratio of partial pressures. Nernst's equation can then be specified somewhat further to yield

$$\mu_e = -4.44 \text{ eV} + 0.029 \text{ eV} [2 \text{ pH} + \log(p_{\text{H}_2}/\text{bar})] \quad (3')$$

for room temperature. This relationship for the chemical potential of the electrolyte is plotted in the inset of figure 3. Also, the position of the valence band maximum for the hydrogen terminated diamond surface ($-\chi - E_g$) at relative to E_{vac} is marked there. It is seen that for typical partial pressures of atmospheric hydrogen of about 10^{-6} mbar and pH values around 6 the chemical potential of the electrolyte lies about 100 meV below the VBM of diamond and electrons from the diamond valence band will be injected into the electrolyte. An aqueous wetting layer as is omnipresent under atmospheric conditions on all surfaces thus fulfills the condition of a sufficiently high electron affinity to act as surface acceptor on hydrogenated diamond. Figure 3 explains also why diamond with a hydrogen terminated surface is unique among all other semiconductors. It is the only one whose ionization energy is low enough to raise the VB of diamond above typical chemical potentials for atmospheric wetting layers. This is essentially a consequence of the low (and in fact negative) electron affinity caused by the surface C–H dipoles [10]. For clean diamond as well as for other semiconductors a number of which are shown in Figure 3 the valence band lies far outside the window accessible by standard atmospheric electrolytes. The electrochemical model presented here thus not only explains why hydrogenated diamond (C:H) shows p-type surface conductivity, but also why this phenomenon is unique among all other semiconductors.

The alignment of the chemical potentials of C:H and an aqueous layer as explained above is the initial situation in the lower panel of figure 4, where the evolution of the hole accumulation layer is sketched schematically. Bringing diamond with a hydrogenated surface into contact with an atmospheric wetting layer leads, as a consequence of the different chemical potentials, to a transfer of electrons out of the diamond valence band into the aqueous phase converting H_3O^+ into $1/2\text{H}_2 + \text{H}_2\text{O}$ (top panel of the figure). This is a self-limiting process since it leaves behind the positive space charge of the holes in the diamond and uncompensated negative ions (HCO_3^-) as space charge in the wetting layer. The corresponding potential raises the energy levels of the electrolyte relative to the diamond bulk and thus tends to equalize the chemical potentials. The final situation is characterized on the right-hand side of figure 4. The initial difference in chemical potentials is now compensated by a potential drop over the hole accumulation layer.

Once surface conductivity has been established the sample can even be put into vacuum and the wetting layer removed. As long as the anions remain at the surface the hole accumulation will also be preserved. One may thus end up in a situation where only charged anions and holes in the valence band of the diamond are left over. In fact, recent cluster calculations performed by Goss *et al* [22] have simulated an isolated HCO_3 radical approaching a hydrogenated diamond surface. As a result a negative charge is indeed transferred into an orbital localized

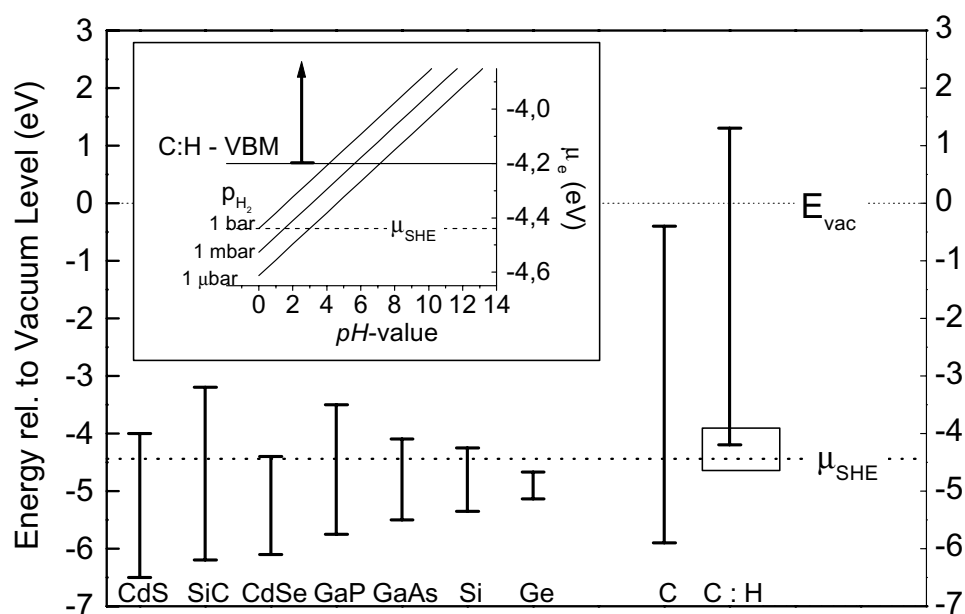


Figure 3. Energies of the band edges of several semiconductors and of hydrogenated and hydrogen-free diamond relative to the vacuum level. The chemical potential μ_{SHE} for electrons in an acidic electrolyte under conditions of the standard hydrogen electrode is marked by the dashed horizontal line. The inset shows the change of the chemical potential μ_e as function of pH value and of hydrogen concentration expressed as partial pressure. Conditions for atmospheric wetting layers are around pH 6 and 1 μ bar.

onto the radical, and the uppermost orbital delocalized inside the diamond cluster becomes unoccupied, reflecting exactly the creation of a hole. One should keep in mind, however, that *isolated* HCO_3^- radicals do not exist in the atmosphere. The calculations can thus only be taken as evidence that the final situation with a negatively charged HCO_3^- ion and a hole in the diamond is energetically stable. In reality it requires the complete electrolytic system at the surface in which the electrical screening of ions by water molecules is the key mechanism that enables the dissociation of acidic species with the subsequent reduction of the oxonium ions to hydrogen. Although subsequent transfer into vacuum can lead to a situation identical to that found as the result of the cluster calculation mentioned above, the electrochemical reaction path seems to be essential in order to establish this situation. The effective electron transfer from the diamond to the surface adsorbates is thus the result of a complex reaction balance. We have used electrochemical, and in fact thermodynamic, arguments to quantify this balance. A theoretical simulation that could validate those arguments would certainly have to consider the complete reaction chain involved and remains a task for the future, maybe for a classical semi-empirical molecular dynamics approach.

Thermal desorption of the anions, which is expected to take place at much lower temperatures than those necessary for surface dehydrogenation in UHV, removes the accumulation layer and leaves a hydrogenated but highly resistive surface. Re-exposing such a surface to the atmosphere restores the original conditions and thus the high surface conductivity. This is exactly what we observe in the experiment illustrated in figure 2. When the hydrogen termination of the surface is destroyed, however, the electron affinity (and the ionization energy) of the diamond has increased so that electron extraction from the valence band into an aqueous

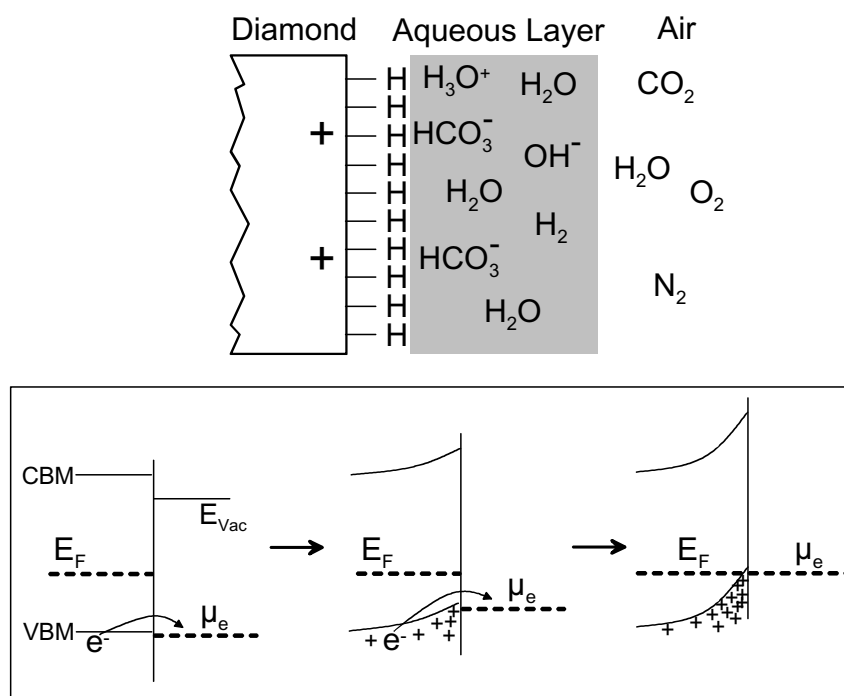


Figure 4. Top: schematic picture of the hydrogenated diamond surface in contact with a water layer as it forms in air. Bottom: evolution of band bending during the electron transfer process at the interface between diamond and the water layer.

atmospheric layer is no longer possible and the basis for the electrochemically induced hole accumulation layer is missing. From equation (3) as plotted in the inset of figure 3 we can also readily understand why the surface conductivity of hydrogenated diamond increases in atmospheres rich in HCl (pH decreases) and is reduced when kept in an NH₃ (pH increases) ambient as observed by Sung Gi *et al* [6]. The former situation reduces μ_e and thus increases the hole accumulation density whereas the latter does the opposite.

Although the electrochemical arguments outlined above can explain why the p-type surface conductivity seems to be unique for diamond, and also why hydrogenation is necessary, we should mention that a direct test of the model with electrolytic solutions with varying pH could only qualitatively confirm the model [23]. Decreasing the pH value of the electrolyte from 13.5 to 4 increased the surface conductivity significantly, however only by a factor of 2, whereas more than four orders of magnitude would have been expected from equations (2') and (3'). In accordance with the authors of [23] we have to assume that chemical equilibrium with respect to electron exchange is not fully reached in the electrolytes tested. For reasons unknown so far the redox reactions finally leaving behind the holes in the diamond apparently take place more effectively in thin atmospheric wetting layers at the surface than in extended electrolytes. Possibly the screening of water molecules in such a thin wetting layer mediates the interaction between atmospheric species and the diamond valence band more directly and more efficient.

Supplementary evidence concerning the role of adsorbates for the surface conductivity of diamond was also given recently by Cannaeerts *et al*. They confirmed the reversible loss of surface conductivity upon mild annealing in vacuum. However, they could already observe

an increase of the conductance of a polycrystalline CVD diamond films by four orders of magnitude after initial hydrogenation in a microwave plasma process without intentional air exposure of the sample. When finally brought into contact with the atmosphere, the conductivity rose further by two orders of magnitude [24]. The authors concluded from their experiments that the role of adsorbates, although being dominant, cannot be exclusive for the surface conductivity, and that another mechanism is active as well. We note, however, that the CVD process used for surface hydrogenation is by far inferior to UHV conditions considering residual impurities in the processing gas. Further experiments seem to be necessary to finally clarify the principal mechanism of surface conductivity on hydrogenated diamond.

4. Conclusions

Based on conductivity measurements and photoelectron yield spectroscopy on hydrogenated diamond surfaces as a function of thermal annealing and exposure to ambient atmosphere, we have developed a new model for the surface conductivity of diamond that suggests a hole accumulation layer at the surface with the corresponding negative charge residing in surface adsorbates. This surface doping mechanism is based on the electrochemical balance between an aqueous, atmospheric surface layer and the diamond. It explains why diamond is the only semiconductor which shows the phenomenon of p-type surface conductivity and also why the hydrogenation of the surface is necessary. The model is supported by recent cluster calculations.

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