

Origin of Surface Conductivity in Diamond

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Hydrogen-terminated diamond exhibits a high surface conductivity (SC) that is commonly attributed to the direct action of hydrogen-related acceptors. We give experimental evidence that hydrogen is only a necessary requirement for SC; exposure to air is also essential. We propose a mechanism in which a redox reaction in an adsorbed water layer provides the electron sink for the subsurface hole accumulation layer. The model explains the experimental findings including the fact that hydrogenated diamond is unique among all semiconductors in this respect.

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Undoped diamond with a gap of 5.5 eV is a bona fide insulator. Yet in 1989 Ravi and Landstrass reported a substantial surface conductivity of hydrogenated diamond surfaces, both of single crystals and of films prepared by chemical vapor deposition (CVD), respectively [1]. These observations have been confirmed over the years [2–5] and the current understanding is as follows [6,7]. The surface conductivity of hydrogenated diamond is of the order of 10^{-4} to $10^{-5} \Omega^{-1}$ at room temperature (RT). The areal density of the *p*-type carriers responsible for the conductivity is about $\rho_S = 10^{13} \text{ cm}^{-2}$ and it is hardly temperature dependent between RT and 150 K. The Hall mobility of the carriers varies also little with temperature ($\sim T^{1.2}$) [8] and is of the order of $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a maximum value of $70 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported for a carrier density of $1.2 \times 10^{12} \text{ cm}^{-2}$ [9]. 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 [10]. The depth distribution of the acceptors responsible for the hole accumulation is discussed controversially, ranging from species at the surface [8,10] over layers extending up to 10 nm into the diamond [6]. It has even been suggested that the acceptors form a layer buried 30 nm below the surface [11]. In the limit of a quasi-two-dimensional acceptor layer at or up to 30 nm below the surface, the observed areal density of 10^{13} cm^{-2} holes requires a band profile such that the surface Fermi level position lies within a few kT at the valence band maximum (VBM) [10]. This surface conductivity is unique among semiconductors and has been utilized to realize a novel type of diamond based field effect transistors [10]. Because the surface conductivity is observed only on hydrogenated diamond surfaces and disappears after dehydrogenation or oxidation of the surface, it has been assumed that hydrogen is directly responsible for the hole accumulation layer by forming particular but as yet unspecified defects that act as acceptors [6]. It is the purpose of the present communication to prove that chemisorbed hydrogen is a necessary but not a sufficient prerequisite for surface conductivity. Hydrogen can thus not be directly responsible for the shallow acceptors needed to generate the hole accumulation layer.

Instead, these acceptors are provided by atmospheric adsorbates. Electrochemical considerations will show that standard atmospheric conditions are perfectly suitable to induce the observed hole accumulation in hydrogenated diamond and will also explain why diamond is special and why this kind of surface conductivity is not observed on any other semiconductor.

We investigated the conductivity of altogether nine diamond samples, namely, four undoped CVD films of variable crystalline quality on silicon substrates, two undoped homoepitaxial layers on single crystals with (100) orientation of type Ib and IIb, respectively, two IIb (100) and (111) single crystals, and one IIa (100) single crystal. The conductivities were measured in air and under ultra-high vacuum (UHV) by placing two gold tips with a distance of 2 mm onto the surface. The quantity we quote is the conductance that was determined from the slope of I-U measurements for $-10 \leq U \leq +10 \text{ V}$. Ohmic characteristics were measured in all cases. Irrespective of the kind of diamond, all samples exhibit conductances between 10^{-6} and 10^{-4} A/V in the hydrogenated state, whereas the low conductance after annealing in air above 300°C or after oxidation in $\text{HNO}_3 + \text{H}_2\text{SO}_4$ was always below 10^{-10} A/V . These conductances are—aside from a geometry factor of order unity—equal to the surface conductivities and the quoted values agree with those reported in the literature for samples with and without surface conductivity, respectively.

In order to elucidate the role of hydrogen, we performed the following experiments. In the first measurement the homoepitaxial (100) diamond layer was introduced in the state of high conductance into UHV. The high conductance was confirmed *in situ* with 10^{-4} A/V and the hydrogenation was established by the fingerprint of negative electron affinity (NEA) of the surface as seen in the total photoelectron yield spectrum [12,13]. After annealing the sample in UHV at $410 \pm 20^\circ \text{C}$ for 15 min, the conductance dropped to 10^{-10} A/V 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 [14]. We then masked half of the sample and removed hydrogen from the other half by

electron beam (1 keV, 0.2 mA/cm², 90 min) induced desorption. This is—unlike thermal desorption—a method to remove hydrogen without introducing in addition electrically active defects as was demonstrated earlier [15]. The corresponding yield spectra are shown in the inset of Fig. 1. The masked area still shows the fingerprint of NEA, namely, a steeply rising electron yield at the band gap energy. This feature is absent on the irradiated surface proving that the hydrogen termination has been removed and the electron affinity turned positive. As also demonstrated in Fig. 1, both halves of the sample are in the low conductance state and remain so as long as they are kept in UHV. However, when they are brought up to air, the conductance of the masked and thus hydrogenated area rises by 4 orders of magnitude within the first twenty minutes of exposure and increases more slowly thereafter until it reaches 10⁻⁵ A/V after three days. By contrast, the dehydrogenated part of the sample remains 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 thermally desorbs in UHV above 400 °C is necessary.

These findings appear to contradict experiments which show that the surface conductivity is *irretrievably* lost if a sample is annealed above ~200 °C in air [9]. According to our results obtained in UHV, one would expect that the conductivity returns upon cooling because the hydrogen termination is expected to be stable up to much higher temperatures. We have therefore investigated the thermal stability of the RT surface conductivity of a plasma hydrogenated IIa C(100) single crystal *in air* while simultaneously monitoring the hydrogen coverage by multiple

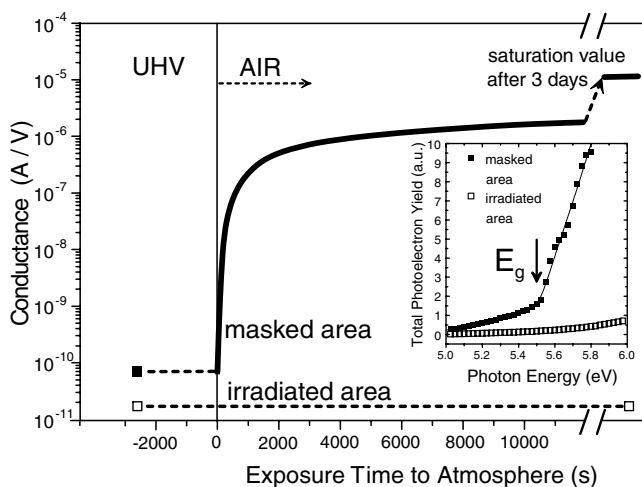


FIG. 1. Surface conductance of the hydrogenated (masked) and the hydrogen-free (irradiated) part of a homoepitaxial diamond (100) layer in UHV and during exposure to air. The inset shows the total photoelectron yield spectra of the two halves before exposure to air. For details see text.

internal reflection infrared spectroscopy (MIRIRS). MIRIRS provides monolayer sensitivity for the C-H stretching vibrations around 2800 cm⁻¹ [16]. The RT conductance of the sample as a function of annealing temperature is plotted in Fig. 2a. Up to 200 °C annealing temperature the conductance remains in the 10⁻⁶–10⁻⁵ A/V range but drops below 10⁻¹⁰ A/V after annealing at 230 °C. The IR signature of the hydrocarbon bonds at the surface is displayed for three selected cases in Fig. 2b. The first spectrum obtained immediately after plasma hydrogenation shows the characteristic stretching mode of the diamond (100) 2 × 1:2H surface at 2896 cm⁻¹ [17] and, in addition, the symmetric (2851 cm⁻¹) and the antisymmetric (2920 cm⁻¹) stretching mode of CH₂ groups of physisorbed *n* alkanes [18]. The spectrum obtained after annealing at 190 °C shows only the monohydride mode characteristic for the surface hydrogen termination but no more hydrocarbon adsorbates. At that stage, the conductance of the sample is still in the 10⁻⁶ A/V range. Hydrocarbon adsorbates are thus

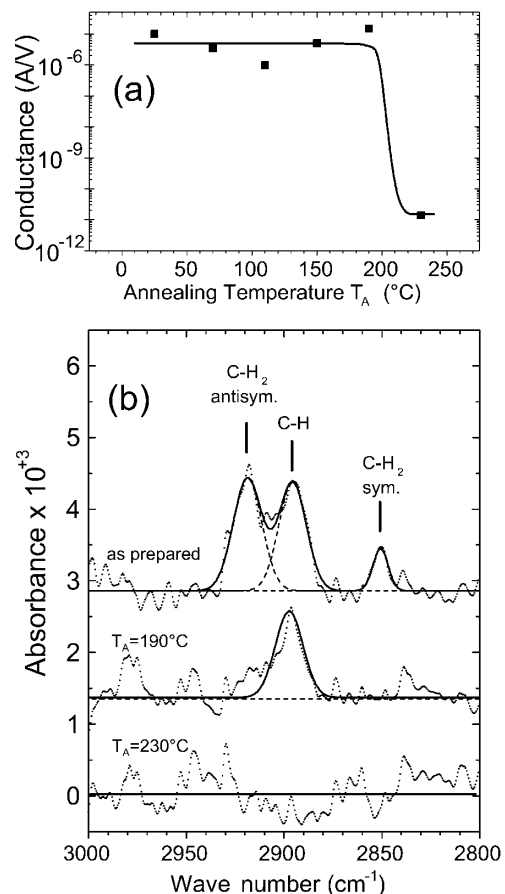


FIG. 2. (a) Surface conductance of a plasma hydrogenated (100) diamond single crystal as a function of annealing temperature in air. (b) Infrared spectra in the region of the C-H stretching modes after the hydrogen plasma treatment and after 190 and 230 °C annealing temperature, respectively. The spectra are offset for clarity.

not responsible for the high surface conductivity. Finally, after the 230 °C annealing step, hydrogen is obviously desorbed from the surface because C-H stretching modes are no longer observed (Fig. 2b). At this stage the conductance of the sample has dropped to 2×10^{-11} A/V. These measurements show that hydrogen desorbs in air at much lower temperatures than in UHV. They also confirm that hydrogen termination is necessary for the high surface conductivity in diamond.

From these results, it appears that an adsorbate from the atmosphere on the hydrogen-terminated diamond surface is required to induce the surface accumulation layer with 10^{13} cm⁻² holes. In order to act as an acceptor, the adsorbate must have its lowest unoccupied electronic level below the VBM of diamond. With an electron affinity $\chi_{C:H} = -1.3$ eV for hydrogenated diamond [19], this requirement sets a lower limit for the electron affinity χ_{ad} of the adsorbate: $\chi_{ad} = E_g - 1.3$ eV = 4.2 eV, where $E_g = 5.5$ eV is the band gap energy of diamond. Electron affinities of molecular atmospheric species lie below 2.5 eV and even for halogen atoms χ_{ad} does not exceed 3.7 eV [20]. Thus, direct electron transfer from the diamond into an atmospheric adsorbate appears to be impossible.

However, a thin water layer, as it forms naturally on all surfaces exposed to atmosphere, provides an electron system which can act as a surface acceptor for diamond. Electron exchange from diamond to the water layer is governed by the redox reaction $2H_3O^+ + 2e^- \rightleftharpoons H_2 + 2H_2O$ [21]. The reaction is driven by the difference in the chemical potential of electrons in the liquid phase (μ_e) and in diamond (Fermi level E_F). As long as μ_e is below E_F , electrons are being transferred from diamond to the water layer and thereby reduce H_3O^+ to H_2 and H_2O . The compensating holes in the diamond form the accumulation layer and the associated space charge induces a potential (surface band bending) that raises μ_e . In equilibrium μ_e and E_F are equal at the interface as shown schematically in Fig. 3. The equilibrium value of μ_e relative to the vacuum level as the common reference for the aqueous layer and the solid [22] depends according to Nernst's equation on the concentrations of $[H_3O^+]$ and $[H_2]$ as

$$\mu_e = \mu_0 - (kT/2) \ln \left[\frac{([H_3O^+]/[H_3O^+]_{SHE})^2}{([H_2]/[H_2]_{SHE})} \right]. \quad (1)$$

Here, $\mu_0 = -4.44$ eV is the chemical potential for electrons under standard hydrogen electrode (SHE) conditions. $[H_3O^+]_{SHE}$ and $[H_2]_{SHE}$ are the oxonium and the hydrogen concentrations of the SHE, respectively. Replacing $[H_2]$ by the H_2 partial pressure p_{H_2} and $[H_3O^+]$ by the pH value of the aqueous layer yields the following at RT for Eq. (1):

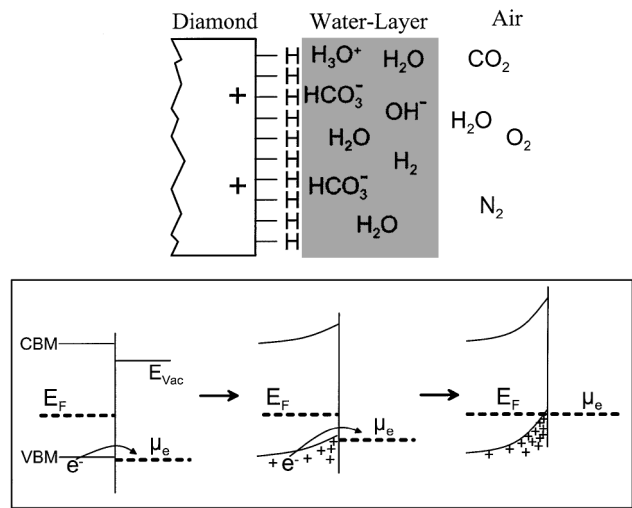


FIG. 3. Top: Schematic picture of the hydrogenated diamond surface in contact with a water layer as it forms in air. Bottom: Evolution of band bending during the electron transfer process at the interface between diamond and the water layer.

$$\mu_e = -4.44 \text{ eV} + \frac{0.058}{2} \text{ eV} \left[2pH + \log \left(\frac{p_{H_2}}{\text{bar}} \right) \right]. \quad (2)$$

This relationship is plotted in the inset of Fig. 4. Because of the CO₂ content in air, standard atmospheric conditions lead to a pH value of water around 6 [23]. With a dissolved hydrogen concentration at the interface in the ppm range which would correspond to a partial pressure of $p_{H_2} \approx 10^{-3}$ mbar, the chemical potential μ_e of an aqueous wetting layer is $\mu_0 + 0.18$ eV = -4.26 eV. Taking the electron affinity of -1.3 eV for hydrogenated

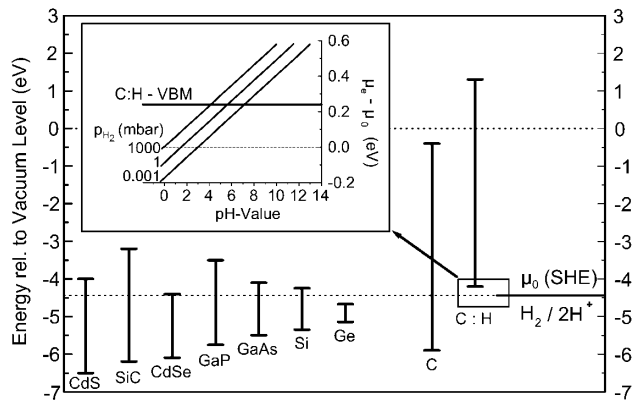


FIG. 4. Energies of the band edges of several semiconductors and of hydrogenated and hydrogen-free diamond relative to the vacuum level. The chemical potential μ_0 for electrons under standard hydrogen electrode (SHE) conditions of -4.44 eV is also given. The inset shows the change of the chemical potential μ_e relative to μ_0 as a function of pH value and of hydrogen concentration expressed as partial pressure. Conditions for atmospheric wetting layers are around $pH = 6$ and $p_{H_2} = 0.001$ mbar.

diamond, the pinning position of E_F at the water/diamond interface lies about 50 meV below VBM (inset of Fig. 4). The hole charge is compensated by those anions (HCO_3^-) that are left uncompensated by the reduction of the oxonium ions. This explains the high surface conductivity of hydrogenated diamond.

Once surface conductivity has been established, the sample can even be put into vacuum and the wetting layer be removed. As long as the anions remain at the surface the hole accumulation will also be preserved. Thermal desorption of the anions which takes place at much lower temperatures ($\approx 300^\circ\text{C}$) than those necessary for surface dehydrogenation in UHV ($\approx 700^\circ\text{C}$) removes the accumulation layer and leaves a hydrogenated but highly resistive surface. An independent measurement of the C1s binding energy on a boron-doped and thus bulk conductive diamond single crystal shows that during such an annealing step the surface Fermi level moves from a position coinciding with the VBM towards midgap by 0.5 eV. On the basis of Eq. (2) as plotted in the inset of Fig. 4, we readily understand why the surface conductivity of hydrogenated diamond increases in atmospheres rich in HCl ($p\text{H}$ decreases) and is reduced when kept in an NH_3 ($p\text{H}$ increases) ambient as observed by Ri *et al.* [24]. The former situation reduces μ_e and thus increases the hole accumulation density whereas the latter does the opposite.

Finally, the electrochemical model presented here explains why hydrogenated diamond is the only semiconductor that exhibits this kind of surface conductivity. According to Fig. 4 the VBM of all semiconductors lies more than 0.7 eV below μ_0 [25]. Standard atmospheric conditions will therefore never produce hole accumulation within those materials. The same is true for nonhydrogenated diamond surfaces. Only via the strong reduction of the electron affinity by hydrogen termination does the VBM of diamond shift up above the chemical potential of typical surface wetting layers.

In summary, we have presented experimental evidence which supports an electrochemical model for the pronounced surface conductivity of hydrogen-terminated diamond. In this model hydrogenation rises the VBM of diamond sufficiently with respect to the vacuum level to place it just above the chemical potential μ_e of a mildly acidic water layer physisorbed at the surface. Electron transfer from diamond to the $\text{H}_3\text{O}^+(\text{H}_2\text{O} + \text{H}_2)$ redox couple accounts for the hole accumulation layer. In equilibrium, the diamond surface Fermi level position E_F^s is pinned at μ_e which coincides essentially with the VBM. Small variations in E_F^s with respect to VBM and

thus variations in conductivity with the $p\text{H}$ value of the wetting layer and the H_2 partial pressure are quantitatively accounted for via Nernst's equation.

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