

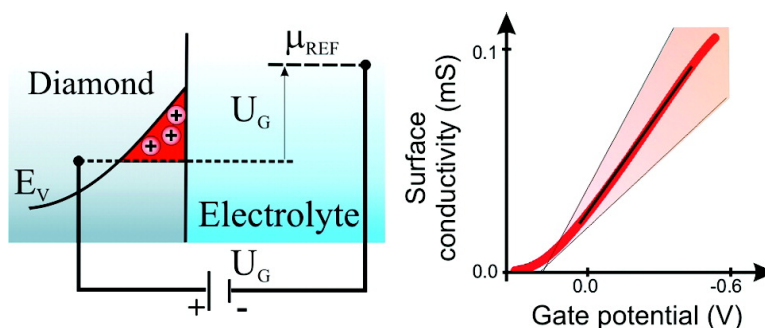
Article

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The Surface Conductivity at the Diamond/Aqueous Electrolyte Interface

Jose A. Garrido,^{*,†} Andreas Härtl,[†] Markus Dankerl,[†] Andreas Reitingner,[†] Martin Eickhoff,[†] Andreas Helwig,[‡] Gerhard Müller,[‡] and Martin Stutzmann[†]

Walter Schottky Institut, Technische Universität München, Garching, Germany, and EADS Innovation Works Germany, EADS Deutschland GmbH, Munich, Germany

Received October 30, 2007; E-mail: garrido@wsi.tum.de

Abstract: We investigate the origin of the surface conductivity of H-terminated diamond films immersed in aqueous electrolyte. We demonstrate that in contrast to the *in air* situation, charge transfer across the diamond interface does not govern the surface conductivity in aqueous electrolyte when a gate electrode controls the diamond/electrolyte interfacial potential. Instead, this almost ideally polarizable interface allows the capacitive charging of the surface. This description resolves the observed disagreement of the pH sensitivity of the diamond surface conductivity in air and in aqueous electrolyte.

Introduction

Since the first report of surface conductivity (SC) in hydrogen-terminated diamond films by Landstrass and Ravi in 1989,¹ different models have been proposed to explain this intriguing phenomenon.^{1–4} The diamond SC, with a value up to 10^{-4} S at room temperature, is characterized by a concentration of holes in the range 10^{12} – 10^{13} cm⁻², with carrier mobilities between 10 and 100 cm² V⁻¹ s⁻¹, or even higher.^{5–7} It was initially suggested that the hydrogenation process resulted in the formation of hydrogen-related shallow acceptor levels, which could explain the observed p-type SC.² However, experiments performed in UHV and air revealed that, in addition to the surface hydrogenation, exposure to air was a necessary condition for the SC.^{3,4} It was also reported that the chemical composition of the atmosphere in contact with the diamond surface strongly influences the SC. Based on these experiments and taking into account the negative electron affinity of H-terminated diamond surfaces,⁸ Maier et al. introduced the transfer doping model.⁴ It was proposed that a redox reaction in an adsorbed water layer, present at any surface in air, provides the electron acceptor level necessary for the accumulation of subsurface holes.⁴ Thus, thermodynamic equilibrium between the electrochemical potential of the electrons involved in the redox reaction and the Fermi level of electrons in the diamond is reached by charge transfer across the diamond/air interface. Maier et al. initially proposed that the H₃O⁺/H₂ redox couple was involved in the

electrochemical reaction.⁴ Together with the wide band gap of diamond, the large negative electron affinity of the H-terminated diamond surface enables the charge transfer between diamond and the adsorbate layer, making this surface conductivity a unique characteristic of H-terminated diamond surfaces. Several groups have investigated the dependence of the SC of diamond films on the acidity/basicity of the atmosphere in contact with the surface and have confirmed the response predicted by the transfer doping model, an increase of the SC for more acidic conditions.^{6,9,10}

Motivated by the expected chemical sensitivity of the diamond SC, different groups have investigated the response of SC H-terminated diamond films immersed in aqueous electrolytes.^{11–13} By using a gate electrode to control the electrochemical potential of the electrolyte, the conductivity at the diamond surface could be modulated, which was used by Kawarada and co-workers to fabricate the first diamond-based solution-gate field effect transistor (SGFET).¹¹ However, it was soon observed that the variation of the surface conductivity with pH did not follow the expected trend predicted by the transfer doping model.^{11–13} Nebel et al. have reported a pH dependence in agreement with the transfer doping model,¹⁴ but we have recently demonstrated that the experimental setup they have used alters the interpretation of their results.¹⁵ Thus, although most experimental results of SC diamond films in aqueous solution are in clear disagreement with the transfer doping model, this

[‡] EADS Deutschland GmbH.

[†] Technische Universität München.

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model has been invoked almost unanimously to explain the SC of H-terminated diamond films operated in aqueous electrolytes.

In this work, we discuss the validity of the transfer doping model for the SC of diamond films immersed in an aqueous electrolyte when a gate electrode is used to control the diamond/electrolyte interfacial potential. We argue that under these conditions no charge transfer across the interface is required to induce the SC and, therefore, the transfer doping model does not hold. Instead, we propose that the almost ideally polarizable diamond/aqueous electrolyte interface allows for the capacitive charging of the surface. This description unifies the observed disagreement of the pH sensitivity of the SC in air and aqueous electrolyte.

Experimental Section

We have investigated surface-conductive H-terminated single-crystalline diamond films. Commercially available (Element Six BV, The Netherlands) natural Ila 100-oriented single-crystalline diamond substrates have been used. The surface roughness was as low as 0.2 nm rms, as determined by AFM measurements. The samples were cleaned in acids in order to remove possible metal contamination, and then chemically oxidized. Finally, the samples were hydrogen-terminated using a hot-filament setup. The samples were heated in a vacuum chamber to a temperature of 700 °C. H₂ was introduced and activated with two 2100 °C hot tungsten wires. The hot sample was exposed to hydrogen radicals for 30 min and cooled in hydrogen atmosphere. Contact angles of around 90° reveal highly hydrophobic surfaces, typical of H-terminated diamond surfaces. More details about the sample preparation can be found in refs 12 and 16. Electrical characterization confirmed a typical value of the surface conductivity on the order of 10⁻⁴ Ω⁻¹. Hall experiments performed in air show carrier concentration of holes of about 10¹³ cm⁻² and mobilities between 50 and 100 cm² V⁻¹ s⁻¹. Solution-gate field effect transistors were fabricated as previously described:^{12,16} Ti/Au contacts were deposited by electron-beam evaporation, acting as drain and source contacts. The 1 × 1 mm² active area between these contacts was defined by oxidizing the sample area outside in an oxygen plasma, leaving just the active area hydrogen-terminated and conductive. Chemically resistant silicone glue was used to prevent direct contact between any metal and the electrolyte, and only the active area was exposed to the solution. The devices were operated as working electrodes in a three-electrode electrochemical cell, consisting of a Ag/AgCl reference electrode and a Pt counter electrode. A commercial potentiostat controls the electrochemical cell. All potential values quoted here are referred to the Ag/AgCl electrode. The sign convention for the gate voltage (U_G) is $U_G = -U$, U being the potential applied to the working electrode with respect to the reference electrode. The standard electrolyte is a 10 mM phosphate buffer solution, with additional 100 mM KCl. Small aliquots of HCl or KOH were added in order to modify the pH of the electrolyte. The electrolyte was partially deaerated 5 min before the experiments.

Results and Discussion

Figure 1 shows the effect of the gate voltage on the surface conductivity. The linear and saturation regimes of the drain-source current together with the modulation of the gate voltage (Figure 1a) resemble the behavior of transistor devices. Figure 1b shows the variation of the surface conductivity with the applied gate potential U_G : For $U_G > 0.3$ V, no surface conductivity was observed. For $0 < U_G < 0.3$ V, the SC increases nonlinearly with U_G , while for $U_G < 0$ V, a linear

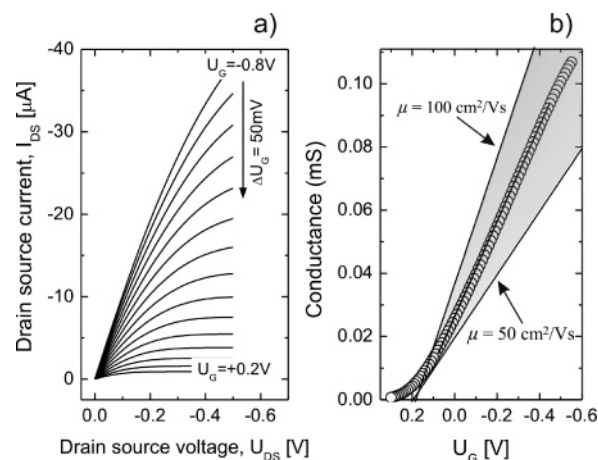


Figure 1. Device characterization of solution gate field effect transistors based on H-terminated surface-conductive single-crystalline diamond: (a) transistor characteristics, showing the drain source current versus the drain source voltage for different gate potentials; (b) variation of the surface conductivity of H-terminated diamond with the applied potential ($U = -U_G$). The surface conductivity disappears for U more negative than -0.3 V. For $U > 0$ V, the surface conductivity increases almost linearly with the applied potential, in agreement with the capacitive charging of the interface described in the text. The shadowed area corresponds to the calculated values of the surface conductivity derived from our model based on the experimentally determined interfacial capacitance of 2 μF/cm² and mobilities between 50 and 100 cm² V⁻¹ s⁻¹. The experimental data (open circles) fit very well within that region.

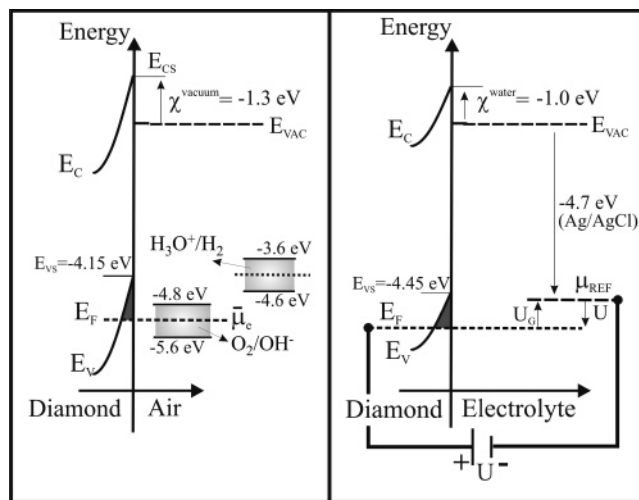


Figure 2. Schematic representation of the energy band diagram of the interface between H-terminated diamond and (a) air or (b) aqueous electrolyte. Both cases show a negative electron affinity as a result of the C–H surface dipole: $\chi = -1.3$ eV in the case of the diamond/air (with adsorbate) interface and $\chi = -1.0$ eV in the case of the diamond/water interface. The position of the valence band maximum at the surface, E_{VS} , is determined by the value of χ . The electrochemical potential for electrons (μ_e) corresponding to the redox reactions of the O₂/OH⁻ and H₂/H₃O⁺ couples are shown in panel a in the pH range from 0 to 14. It is assumed that in thermodynamic equilibrium, reached by charge transfer across the interface, the Fermi level is aligned with the μ_e of the O₂/OH⁻ electrochemical reaction. In the case of operation in aqueous electrolyte, all applied voltages are referred to the level of the reference electrode (μ_{REF}). A positively applied potential (U) with respect to the reference electrode induces the hole accumulation at the diamond surface.

increase is observed. In the following, band diagrams of diamond surfaces will be discussed in order to understand the gate voltage dependence of the SC. The energy levels are given with respect to the vacuum reference. Figure 2a represents the currently accepted description of the hydrogenated-diamond/

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air interface, with a negative electron affinity of $\chi^{\text{vacuum}} = -1.3$ eV, as measured in a vacuum.⁸ The position of the valence band maximum at the surface (E_{VS}) is determined by χ^{vacuum} and the band gap, so $E_{\text{VS}} = -(E_{\text{G}} + \chi^{\text{vacuum}})$, with $E_{\text{G}} = 5.45$ eV and $E_{\text{VS}} = -4.15$ eV. Maier et al. have suggested that under a slightly acidic atmospheric condition (pH = 6), the electrochemical potential for electrons ($\bar{\mu}_{\text{e}}$) involved in the redox reaction $\text{H}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{e}^-$ was about 4.26 eV below the vacuum level, and thus was an acceptor level for electrons from the diamond valence band.⁴ However, the value of the electron affinity measured in a vacuum is most likely different than that in air. Piantanida et al. have estimated the contribution of a monolayer of water molecules to the surface electron affinity using basic electrostatic considerations and tabulated values of electronegativity of C, H, and H₂O.¹⁷ They reported that the electron affinity in the presence of water was increased by +0.8 eV, which would result in a total value of $\chi^{\text{water}} = -0.5$ eV. However, this model assumes all interfacial water molecules to be equally oriented,¹⁷ neglecting the very important microscopic structure of the water at the diamond interface,¹⁶ as will be discussed below. In any case, the presence of water is expected to modify the value of the electron affinity and, thus, the position of E_{VS} . It was proposed that due to the position of E_{VS} more negative than -4.26 eV, other redox couples involving oxygen (for instance, the O_2/OH^- redox couple, $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$ in Figure 2a) were more likely to be responsible for the SC effect.⁹ To the best of our knowledge, the exact nature of the electrochemical redox couple remains unclear.

A different situation arises in the case of H-terminated diamond surfaces immersed in an aqueous electrolyte when the potential at the diamond/electrolyte interface is determined by active control with a potentiostat (Figure 2b). In this situation, the potentiostat forces a new equilibrium by fixing the potential drop between E_{F} in the diamond sample and the reference electrode. Therefore, no thermodynamic equilibrium exists between E_{F} and the redox couple responsible for the SC in air. For increasing negative gate potentials U_{G} , the position of E_{F} is driven further below the valence band maximum, increasing the accumulation of holes at the diamond/electrolyte interface. In contrast, if the applied potential is reversed and more positive gate potentials are applied, E_{F} at the diamond surface will be pushed eventually above the valence band maximum, and the SC channel will finally disappear. Indeed, this is in agreement with our experiments, as shown in Figure 1b. In a first approximation, the position of E_{VS} can be derived from the conductivity– U_{G} curve, assuming that when $E_{\text{F}}(U_{\text{G}}) = E_{\text{VS}}$ no accumulation of carriers occurs at the surface of diamond and the SC vanishes. From Figure 1b, we estimate that this occurs when E_{VS} is about 0.2–0.3 V more negative than the reference electrode (-4.7 eV), so E_{VS} is between 4.4 and 4.5 eV below the vacuum level, E_{VAC} . Therefore, the electron affinity of the H-terminated diamond surface immersed in an aqueous electrolyte can be estimated by $\chi^{\text{water}} = -(E_{\text{VS}} + E_{\text{G}}) \approx -1.0 \pm 0.5$ eV. In Figure 2b we have used $\chi^{\text{water}} = -1.0$ eV, which is significantly higher than the value of -0.5 eV predicted by Piantanida et al.¹⁷ This is not surprising, since we do not expect all the water molecules with the same orientation at the surface,

as assumed in ref 17. We have recently performed detailed molecular dynamics (MD) calculations of the H-terminated diamond/water interface and demonstrated that, due to hydrophobic interactions, water molecules are partially oriented in the first few layers.¹⁶ This is not a unique characteristic of diamond, but results from the hydrophobic nature of the H-terminated surface.¹⁸ The partial orientation of the water molecules induces a nonzero interfacial dipole which enters in the calculation of the electron affinity, $\chi^{\text{water}} = \chi_{\text{C-C}} + e\psi_{\text{C-H}} + e\psi_{\text{water}}$. The second term in this equation corresponds to the C–H interfacial dipole, which together with the first term (corresponding to the electron affinity of a clean reconstructed diamond surface) amounts to a value of -1.3 eV. From the MD calculations reported in ref 16, the expected value for the contribution of the ordered water molecules is about $e\psi_{\text{water}} = +0.4$ eV. Therefore, the expected value of $\chi_{\text{theo}}^{\text{water}} = -0.9$ eV is in agreement with the value estimated from our experiments, $\chi_{\text{exp}}^{\text{water}} = -1$ eV. However, we would like to point out that this value of the electron affinity depends on the quality of the surface hydrogenation and can also depend on the pH if hydroxide ions adsorb at the surface.¹⁶

In the description of the modulation of the SC with the applied potential, we have not mentioned the process of charge transfer across the interface as a mechanism for the formation of SC. Instead, we have described a situation in which the SC is induced by capacitive polarization of the interface. Assuming an ideally polarizable diamond/electrolyte interface, that is, no charge transfer is allowed across the interface,¹⁹ the application of the potential between the solution and the diamond surface provides the required positive charges at the interface. The assumption of ideal polarizability of the diamond surface is completely justified in this case, because the applied potentials are within the electrochemical potential window of diamond. In this potential region, Faradaic current across the diamond/electrolyte interface was not observed. We have performed electrochemical impedance spectroscopy measurements at the hydrogenated-diamond/electrolyte interface revealing that in the potential region $+0.1 < U < +0.8$ V, the interface behaves almost like an ideal capacitor, with a value of about $C_1 = 2$ $\mu\text{F}/\text{cm}^2$.²⁰ Thus, the surface conductivity can be calculated as $\sigma = q\mu p$, where μ represents the hole mobility and p the hole carrier density. Using our simplified description of the interface, we can therefore calculate p from the voltage drop at the interfacial capacitance C_1 , $p = C_1 U_1 / q$. This interfacial voltage U_1 can be related to the applied gate potential by $U_1 = -U_{\text{G}} + U_{\text{k}}$, being U_{k} a constant taking into account the threshold voltage and the effect of possible adsorbed surface charge.¹⁶ Thus, the total conductivity can be written as $\sigma = \mu C_1 (-U_{\text{G}} + U_{\text{k}})$, which predicts a linear dependence between the conductivity and the applied potential, with a slope given by the product μC_1 . Figure 1b shows the variation of the surface conductivity as a function of the applied potential (same device as in Figure 1a), confirming the linear dependence for gate potentials below 0 V. We have calculated the slope of such a dependence for a series of devices, and the resulting averaged value of the slope is $(-1.35 \pm 0.15) \times 10^{-5}$ S/V. Using the measured value of $C_1 = 2$ $\mu\text{F}/\text{cm}^2$ and standard values of the mobility between 50 and 100 $\text{cm}^2 \text{V}^{-1}$

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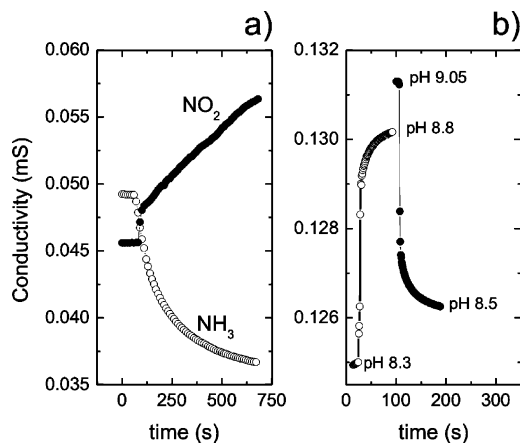


Figure 3. Response of the surface conductivity upon changes of the chemical and electrochemical environment. Panel a summarizes the results of the in-air experiment, showing the effect of NO₂ and NH₃ on the SC in a synthetic air atmosphere. The addition of 50 ppm NO₂ results in a SC increase (solid symbols), while 5000 ppm of NH₃ induces a SC decrease. As discussed in the text, NO₂ and NH₃ are expected to decrease and increase the pH of the adsorbed water layer, respectively. The slow response is the result of the slow kinetics of charge transfer across the interface. Panel b corresponds to the in-electrolyte experiment, showing the SC response upon pH changes. The experiment was performed in a 90 mM KCl/10 mM PBS buffer, with $U_G = -0.5$ V and $U_{DS} = -100$ mV. The pH was modified by the addition of HCl or KOH. The SC increases with increasing pH, which is the opposite of the result observed in air. Furthermore, the response is much faster compared with the in air situation.

s^{-1} , the theoretical prediction of the slope is $(-1.5 \pm 0.5) \times 10^{-5}$ S/V, in excellent agreement with the experimental results. The shadowed area in Figure 1b represents the theoretical values of the surface conductivity expected from our description of the SC, assuming mobilities between 50 and 100 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. There we have used a value of $U_k = 0.2$ V, which can be assigned to the threshold voltage of the device. So far, we have assumed a constant value of the carrier mobility, independent of the applied gate potential. Recent in-liquid Hall-effect experiments revealed that this assumption is not completely valid.²¹ However, the required small corrections do not alter the overall description presented here.

To further demonstrate the different response of the SC in air (when the transfer doping model can be applied) and in liquid, we have investigated the time transients of the SC upon changes in chemical and electrochemical environment. Figure 3a displays conductivity transients of a surface-conductive H-terminated diamond sample exposed to an atmosphere consisting of synthetic air to which NO₂ or NH₃ are added. A more detailed description of these gas-sensing experiments has been given recently.¹⁰ Upon exposure of the diamond sample to a NO₂-containing atmosphere, a slow increase of the SC was observed. The opposite effect was observed when NH₃ was used, which induces a SC decrease. These results can be rationalized using the transfer doping model description of the SC as follows. Under the conditions of these experiments (in air, without any gate potential control), the modification of the SC upon variations of the chemical environment results from the effect of the added gases on the electrochemical potential of electrons ($\bar{\mu}_e$) in the adsorbed water layer. Thus, NO₂ increases the acidity of the adsorbed water layer, as expected from its reaction with water: $\text{NO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{H}_3\text{O}^+ + \frac{1}{2}\text{H}_2$. In contrast,

NH₃ produces the opposite effect as its reaction with the adsorbed water releases hydroxide ions, $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$. Therefore, while NO₂ is expected to decrease the pH of the adsorbed water layer, NH₃ will increase the pH.¹⁰ As discussed before, the transfer doping model assumes thermodynamic equilibrium between E_F in the diamond and $\bar{\mu}_e$ of electrons involved in the reaction of the redox couples $\text{H}_3\text{O}^+/\text{H}_2$ or O_2/OH^- . As can be understood from Figure 2, a decrease of pH will move $\bar{\mu}_e$ further down, forcing E_F deeper into the diamond valence band; as a result the surface conductivity increases. The opposite occurs when the pH increases; the SC decreases. The effect of NO₂ and NH₃, as shown in Figure 3a, is in agreement with this explanation. Interestingly, the response of the SC to NO₂ and NH₃ is very slow, as expected from the slow kinetics of electron transfer across the diamond/water interface. Using metal-oxide gas sensitive devices (results not shown here), we have confirmed that the adsorption of gas molecules is very fast and does not limit the sensing mechanism, in agreement with previous reports.²² The response of the SC to a variation of the pH of the electrolyte is shown in Figure 3b. In contrast to the in air situation, a decrease of the pH results in a SC decrease, which is opposite to that expected from the transfer doping model. In addition, the transient upon pH changes is much faster than in the case of the in air experiment (Figure 3a). These results indicate that when a SC diamond device is operated in an electrolyte with a gate potential control, the variation of the SC upon pH variations does not occur due to charge transfer across the diamond interface. Instead, other pH sensitivity mechanisms must be invoked. We have previously discussed how using a description of the diamond/water interface based on the site-binding model²³ can allow explanation of the correct pH dependence.¹² In addition, the adsorption of OH⁻ and H₃O⁺ ions onto the H-terminated diamond surface¹⁷ could also explain such pH dependence. However, a detailed microscopic understanding of the pH sensitivity of diamond surfaces is still missing and not within the scope of this paper.

Conclusions

In summary, we have presented a description of surface-conductive H-terminated diamond devices operated in electrolyte with a gate potential control. We suggest that under the control of a gate electrode with a potentiostat and in certain potential range, the diamond/electrolyte interface behaves like an almost ideal capacitor, allowing the capacitive charging of the interface. Our model agrees very well with the measured gate voltage dependence of the surface conductivity. In addition, we report how the pH dependence of the SC differs for in air and in liquid operation. While the transfer doping model applies for the operation in air, the pH response for in liquid operation cannot be explained by that model. The very different time constants of the responses observed under in air and in liquid operation support the suggestion of two different charging mechanisms at the diamond surface: (i) electron transfer across the interface, as suggested by the transfer doping model, for in air operation and (ii) capacitive charging, in which no charge transfer across the interface is required, for a gate-controlled in liquid operation. Interestingly, a SC diamond electrolyte gate field effect transistor

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behaves like a MOSFET device (with the metal replaced by the solution gate) in which there is no insulating layer preventing carriers crossing the interface. A similar conclusion has been recently reached by Song et al.²⁴ Here we suggest that the very slow kinetics of electron transfer at the diamond/electrolyte interface play the role of the insulating barrier. Finally, our description resolves the observed disagreement of the pH

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sensitivity of the diamond surface conductivity in air and in aqueous electrolyte.

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