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*p*H sensors based on hydrogenated diamond surfaces

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We report on the operation of ungated surface conductive diamond devices in electrolytic solutions. The effect of electrolyte *p*H on the channel conductivity is studied in detail. It is shown that fully hydrogen terminated diamond surfaces are not *p*H sensitive. However, a pronounced *p*H sensitivity arises after a mild surface oxidation by ozone. We propose that charged ions from the electrolyte adsorbed on the oxidized surface regions induce a lateral electrostatic modulation of the conductive hole accumulation layer on the surface. In contrast, charged ions are not expected to be adsorbed on the hydrogen terminated surface, either due to the screening induced by a dense layer of strongly adsorbed counter-ions or by the absence of the proper reactive surface groups. Therefore, the modulation of the surface conductivity is generated by the oxidized regions, which are described as microscopic chemical in-plane gates. The *p*H sensitivity mechanism proposed here differs qualitatively from the one used to explain the behavior of conventional ion sensitive field effect transistors, resulting in a *p*H sensitivity higher than the Nernstian limit. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1866632]

Hydrogen-terminated diamond surfaces have recently received much attention due to their potential use as transducer elements in biosensing devices. The functionalization of H-diamond surfaces with DNA oligonucleotides has been successfully demonstrated in a pioneering paper by Yang *et al.*, pointing out that diamond thin films can be used as stable and selective platforms onto which biomolecules can be integrated.[1] In addition, our group has recently reported the operation of enzyme-based nanocrystalline diamond electrodes.[2] These reports confirm the superior chemical stability of diamond films compared, for instance, to gold, glass, or silicon, which are conventionally employed as substrates for biomolecule attachment.

Complementing the outstanding properties of diamond as an interface to biological systems, and in order to fully exploit the potential of diamond in the biosensor area, different detection schemes have yet to be developed to transduce biochemical reactions into electronic signals. Ion-sensitive field effect transistors (ISFETs) have been combined with biological receptors (enzymes, oligonucleotides, and cells), and can be considered as a basic building block of microelectronic biosensors.[3–5] So far, there have only been a few reports investigating the applicability of diamond-based ISFET devices.[6–8] The *p*-type conductive layer which is induced at the diamond surface by a hydrogen termination has been suggested as a very promising sensing system to be used in a liquid electrolyte environment. For example, modified H-terminated diamond surfaces have been reported to be sensitive to Cl^- and Br^- ions.[7] However, the sensitivity of diamond surfaces to changes in the *p*H of the electrolyte solution is still elusive.[6] "Conventional" ISFETs are based on an insulator(oxide)/semiconductor multilayer system, and their *p*H sensitivity is attributed to changes of the insulator surface potential which results from ion adsorption/desorption at reactive oxygen surface groups.[9] As will be discussed in this letter, surface conductive diamond ISFETs can be fabricated using an alternative design. We will show how the existence of a quasi-two-dimensional conductive path at the H-terminated diamond surface can lead to new detection schemes which have advantages compared to conventional ISFETs.

This letter describes the operation of H-terminated diamond devices in electrolytic solutions. The effect of the *p*H value on the surface conductivity is discussed in terms of oxygen-induced reactive surface sites which act as microscopic in-plane chemical gates. *p*H sensitivities higher than 59 meV/*p*H, the Nernst limit, are reported.

Devices were fabricated on nonpolished free-standing polycrystalline diamond substrates which were prepared by microwave plasma assisted chemical vapor deposition. The thickness of the diamond films varied between 200 μm and 1 mm, the area was about 4×4 mm^2. Prior to hydrogenation and in order to remove any nondiamond component at the substrate surface, the diamond samples were cleaned in CrO_3/H_2SO_4 during 1 h at 180 °C, followed by a H_2O_2 solution (30% concentrated) for 15 min. The previous cleaning process induces an oxygen termination of the diamond surface. In a final step, samples were hydrogenated in a microwave plasma for 5 min at 500 °C. Room temperature Hall experiments were performed to evaluate the electronic properties of the surface conductivity. It was found that the surface conductivity is typically characterized by a concentration of holes in the range of 5×10^{12}–5×10^{13} cm^{-2} with mobilities varying between 10 and 140 cm^2 V^{-1} s^{-1}.[10]

Devices were fabricated by standard photolithography processing in combination with oxygen plasma isolation to define the active area, which is about 3×3 mm^2. Ti(200 Å)/Au(2000 Å) contacts were deposited as drain and source contacts using electron-beam evaporation. The processed diamond substrates were mounted in a ceramic holder, and the drain and source metal contacts were bonded

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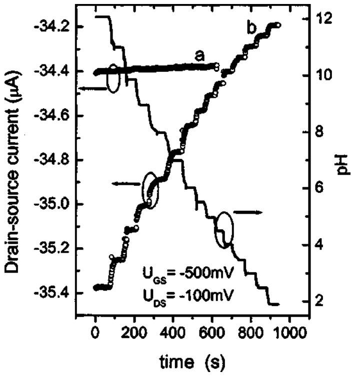

FIG. 1. Variation of I_{DS} with the pH of the electrolyte for a hydrogen-terminated diamond device (curve a) and for an ozone-treated device (curve b). The potential of the electrolyte was fixed by a potentiostat at −0.5 V with respect to the source contact.

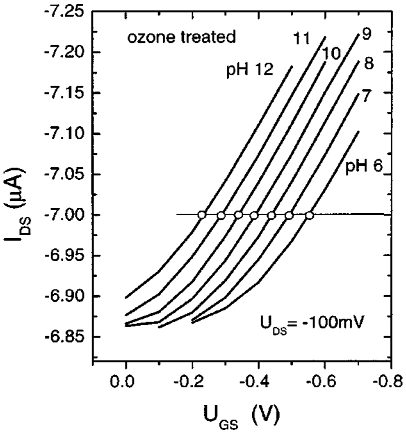

FIG. 2. I_{DS}–U_{GS} curves of an ozone-treated device as a function of the electrolyte pH.

to Au metal pads evaporated on the ceramic holder. To prevent any contact between the metal regions and the electrolyte, chemically resistant silicone glue was employed to cover the metal contacts and pads. The gate area exposed to the electrolyte is the same as the active area, i.e., 3×3 mm^2.

The ceramic holder with the diamond device was used as the working electrode in a three-electrode electrochemical cell, equipped with a Ag/AgCl (3M saturated KCl) reference electrode and a Pt wire counter electrode. A commercial potentiostat (BANK LB81M) was used to control the electrode potentials. The experimental setup allows the simultaneous recording of the drain–source and the gate(electrolyte)–source voltage. All the potential values are referred to the Ag/AgCl electrode.

The electrochemical cell is also equipped with a pH meter and a thermometer. A stirrer guarantees a homogeneous electrolyte environment. All experiments were performed in a 100 mM KCl saline solution buffered with a phosphate buffer (10 mM), which allows a controlled pH change in the range from 2 to 12.

The pH value of the KCl electrolyte was varied by titration with potassium hydroxide (KOH) or sulphuric acid (H_2SO_4), and was monitored with a calibrated pH meter. To induce a pH sensitivity, H-terminated surfaces were modified by means of a mild ozone treatment. Ozone was generated by a commercial system (Sander Lab-Ozonisator) using arc-discharges. During the ozone treatment, which was performed at a temperature of about 90 °C, the surface conductivity was monitored by measuring the drain–source current at a fixed drain–source voltage of −100 mV. The ozone treatment duration was varied between 1 min and hundreds of minutes, which produces a variation of the sample conductivity between 10^{-4} and 10^{-6} Ω^{-1} cm^{-1}.

The drain–source current (I_{DS}) was measured while the electrolyte was titrated and the pH varied between 3 and 10. During the experiments the value of the applied drain–source voltage was −100 mV, and the gate-source (U_{GS}) voltage was kept constant at −500 mV. Curve a in Fig. 1, which depicts a plot of the I_{DS} versus time as a function of pH shows the result obtained in a device which was not treated with ozone, and therefore with a H-terminated surface. No noticeable or only a very small variation of I_{DS} was typically observed in devices with a H-terminated surface. However, after the devices were treated with ozone, an evident change of the drain–source current versus pH was observed, as shown in Fig. 1 (curve b). The response of the device to the change in the pH is almost immediate, without a significant drift of the drain–source.

The sensitivity of an ISFET is normally given in terms of the change of the gate potential equivalent to a change of pH, $\partial U_{GS}/\partial p\text{H}$,[9] and can be extracted from the set of I_{DS}–U_{GS} curves depicted in Fig. 2, which shows the I_{DS}–U_{GS} dependence of an ozone-treated device at different pH values. Figure 3 compares the pH sensitivity of diamond devices before (as-hydrogenated) and after the ozone treatment. In general, no pH sensitivity was observed in H-terminated diamond devices which were not treated with ozone. However, we have also found that nominally H-terminated devices with a poor conductivity (which can be attributed to a nonoptimum hydrogenation process) showed low pH sensitivity, typically about 25 mV/pH. In contrast, the surface modification induced by the ozone treatment gives rise to a clear linear pH sensitivity in the pH range from 2 to 10 [curve c in Fig. 3]. Further exposure of the device surface to ozone results in an increase of the pH sensitivity [curve d in Fig. 3]. Surprisingly, the pH sensitivities reported in Fig. 3, 63 and 72 mV/pH, are larger than the theoretical maximum predicted by the Nernst limit, which is 59.2 mV/pH.[9]

In order to understand the experimental results it is important to consider the peculiarities of these diamond devices. As explained before, hole accumulation occurs underneath the hydrogen-terminated diamond surfaces. Therefore, when immersed in an electrolyte the large density of accu-

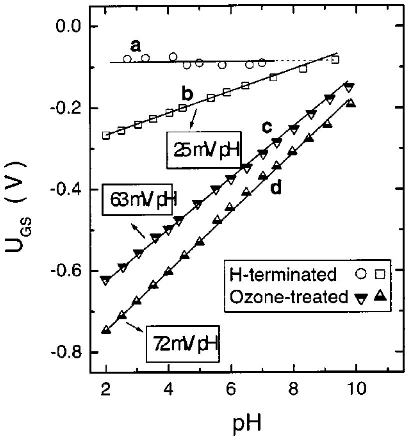

FIG. 3. pH sensitivity (mV/pH) of freshly hydrogenated devices (curve a and b) compared to ozone–treated diamond devices (curve c and d).

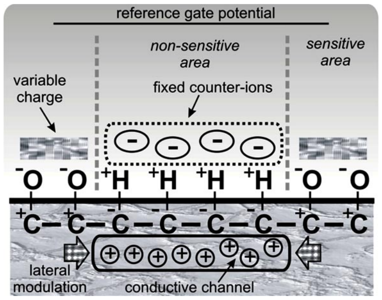

FIG. 4. Microscopic view of a device cross section in which a H-terminated region is embedded between two O-terminated regions. Holes are only accumulated under the H-terminated diamond surface. Varying the pH modifies the adsorbed charge only at the oxidized regions, inducing a lateral modulation of the conductive channel.

mulated holes in the diamond will be counterbalanced by a dense layer of adsorbed ions (see Fig. 4).[11] On the other hand, there is no hole accumulation at the non-H-terminated surfaces (i.e., in the oxygen terminated regions). In the case of hydrogen-terminated diamond surfaces, none or very low pH sensitivity has been measured, which might indicate that the density of adsorbed counter-ions is mainly determined by the amount of accumulated holes. Therefore, changes in the pH of the electrolyte are then screened by the adsorbed counter-ions. A different explanation could be based on the assumption that there are no reactive groups at the H-terminated surfaces which can interact with protons in the solution. Both situations lead to the same result: H-terminated surface areas can be considered as nonsensitivity regions, as confirmed by the experimental results. On the other hand, at oxidized regions (referred to in Fig. 4 as *sensitive areas*) the pH of the electrolyte is able to modulate the amount of adsorbed surface charge. Similar to the site binding model for the SiO_2/electrolyte interface,[12] the presence of hydroxyl groups at the oxidized diamond surfaces can result in neutral surface groups (C–OH), negatively charged groups ($C-O^-$), or positively charged groups ($C-OH_2^+$), depending on the concentration of protons in the solution. In addition to the so-called potential determining ions (H^+ and OH^-), the formation of surface complexes between counter-ions in the electrolyte and charged surface groups ($C-O^-$ or $C-OH_2^+$) can also contribute to the total surface charge.[13] Thus, changing the electrolyte pH changes the concentration of protons in solution, which can be adsorbed at the O-terminated regions, giving rise to a lateral depletion of the conductive channel. The larger the concentration of protons (lower pH), the higher the number of protons adsorbed at the oxidized regions, increasing the lateral depletion of the conductive channel and, hence, decreasing the drain–source current, as shown in Fig. 1. Therefore, pH sensitivity is expected only after the generation of oxidized regions (*sensitive areas*) by the ozone treatment, in agreement with our results. Hydroxyl groups have been reported to be present at the surface of oxidized 111-oriented single crystalline diamond layers.[14] Confirming this result, the large hydrophilicity observed in oxidized polycrystalline diamond surfaces has been attributed to the presence of hydroxyl groups at the 111-oriented facets of the polycrystalline material.[15]

The above-described pH sensitivity mechanism differs from the one employed to explain the behavior of “conventional” ISFETs based on an insulator/semiconductor structure,[8] in which electrochemical processes of ion adsorption/desorption are directly transduced into a homogeneous potential change at the device surface. This potential change, which follows the Nernst equation, modulates the channel conductivity under the insulator layer. From a device point of view, the surface potential directly translates into a threshold voltage variation.[9] Thus, the pH sensitivity is measured as a shift of the $I_{DS}-U_{GS}$ curves, similar to the one observed in Fig. 2, with a maximum sensitivity of 59.2 mV/pH. In contrast, for surface conductive diamond ISFETs it is not possible to establish such a straightforward relation between the surface potential modulation induced by ion adsorption at the oxidized regions and the surface conductivity in the neighboring hydrogenated regions. The modulation of the surface potential at the oxidized regions, which is induced by ion adsorption, is still governed by the Nernst equation. However, the coupling between this surface potential and the conductive channel can lead to the supra-Nernstian pH sensitivity observed in Fig. 3, depending on the percolation behavior of the interconnected conductive H-terminated regions between the source and drain contacts.

Summarizing, we have studied the behavior of H-terminated diamond surface transistors operating in electrolytic solutions. Our results show that fully H-terminated diamond surfaces are not sensitive to changes of the pH. In contrast, H-terminated surfaces modified with C–O bonds by means of ozone-treatment show clear pH sensitivity. Charge adsorbed on O-terminated sensitive areas is able to modulate the conductivity of the neighboring H-terminated conductive channels by electrostatic interactions. Oxidized regions thus act as lateral chemical in-plane gates which give rise to supra-Nernstian pH sensitivity.

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