

Diamond—electrolyte interfaces: The role of hydrophobicity

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Biosensor and bioelectronic devices are still a matter of intensive research and their commercial success remains a challenge. Interfaces with water play a major role in these devices. Hydrogen-terminated diamond is known to be surface conducting and hydrophobic when in contact with water. While the hydrophobic interaction of surfaces with water is a well-known phenomenon, there is not much known on its influence on biosensor devices. In contrast to silicon, diamond does not have a native oxide. Thus its two-dimensional hole gas (2DHG) is located very close to the electrolyte which acts as a gate. The sensing signals are generated by potential changes across the solid—liquid interface. Using the nextnano³ software [1], we model the hydrophobic interaction and charge accumulation at the hydrogen-terminated diamond—aqueous electrolyte interface by self-consistently calculating the interfacial potential and the ion charge accumulation in the electric double layer as a function of electrode gate potential [2]. The hole carrier distribution in diamond is described by a 6×6 $\mathbf{k}\cdot\mathbf{p}$ model. We show that experimental results on the sheet charge density of diamond field-effect devices can be reproduced by our simulations, only if we include the hydrophobic nature of the surface into our model. The hydrophobic model employed in our work is derived from molecular dynamics simulations. This so-called extended Poisson—Boltzmann model takes into account a spatially varying dielectric constant in the electrolyte based on the calculated density of water at the interface, as well as repulsive potentials of mean force (PMF) for each ion species [3].

In order to quantitatively understand the modulation of the 2DHG density by varying the electrolyte potential, we analyze the charge distribution at the solid—liquid interface

in more detail. Fig. 1 shows the calculated valence band edge energy (black lines) of the hydrogen-terminated diamond—electrolyte interface for an applied gate voltage $U_G = -0.2$ V. By adjusting the gate potential applied between the reference electrode in the electrolyte and a contact on the diamond, one can shift the valence band edge with respect to the Fermi level ($E_F = 0$ eV) in diamond. This modifies the confinement potential of the resulting triangular well, and thus also the positive charge density (blue lines) of the 2DHG in the diamond, leading to a band bending at the surface. The hole density is mirrored by the corresponding total ion charge density (net negative charge) in the electrolyte indicated in red. The results of the standard Poisson—Boltzmann (PB) calculation are

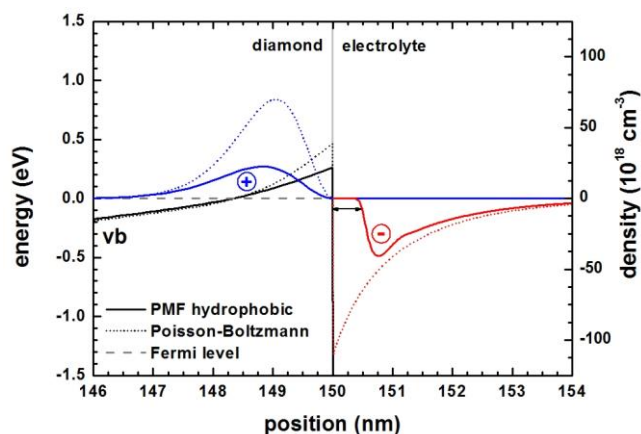


Fig. 1: Calculated valence band edge energy (black lines) of the diamond—electrolyte interface. The positive hole charge density (blue lines) of the 2DHG in the diamond is mirrored by the corresponding total ion charge density (net negative charge) in the electrolyte (red lines). The results of the standard Poisson—Boltzmann calculation (dotted lines) are compared to our new extended Poisson—Boltzmann model (solid lines) that takes into account the hydrophobic interface. The arrow indicates the region of low water density (hydrophobic region).

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shown in dotted lines whereas the results obtained with our new extended Poisson–Boltzmann model that takes into account the hydrophobic interface are shown in solid lines. The arrow indicates the region of low water density (hydrophobic region) which has a width of approximately 0.3 nm. This region acts as a small insulating layer with a low dielectric constant.

The experimental carrier concentrations for different gate potentials from in-liquid Hall effect measurements and the simulated results obtained with our calculations are compared in Fig. 2. The experimental data sets for several (100) diamond samples are normalized with respect to their threshold voltage. Above the threshold voltage all of them show a nearly linear increase of the carrier concentration with the gate potential U_G . The slope of the experimental data points is almost the same for all samples. From the slope one can determine the interfacial capacitance to be about $2 \mu\text{F}/\text{cm}^2$. The extended Poisson–Boltzmann model for the hydrophobic interface (black solid line), the hydrophilic interface (red dashed line) and the conventional Poisson–Boltzmann model (blue dash-dotted line) are compared. The agreement between the hydrophobic extended PB model and the slope of the experimental data is remarkable. In order to test the influence of the size of the water-depleted region, we have shifted the water density profile by a tiny amount of $\pm 0.05 \text{ nm}$ with respect to the surface. These calculations (dash-dot-dot and dot) show that our assumed water density profile works surprisingly well.

In conclusion we have demonstrated that the hole accumulation at the hydrogen-terminated diamond–electrolyte interface can be simulated to great accuracy with the extended Poisson–Boltzmann model where the hydrophobic character of the surface is explicitly taken into consideration. Hydrophobicity limits the approach of electrolyte ions and water to the surface and therefore increases the potential drop in the electrolyte. This reduces the effective potential at the semiconductor surface. Consequently, the sensitivity of potentiometric biosensor devices which depend on the variation of the number of charge carriers with potential change is profoundly affected by the modification of the interfacial capacitance for any hydrophobic surface.

- [1] <http://www.nextnano.de/nextnano3>
- [2] M. Dankerl, A. Lippert, S. Birner, E. U. Stützel, M. Stutzmann, and J. A. Garrido, *Physical Review Letters* **106**, 196103 (2011)
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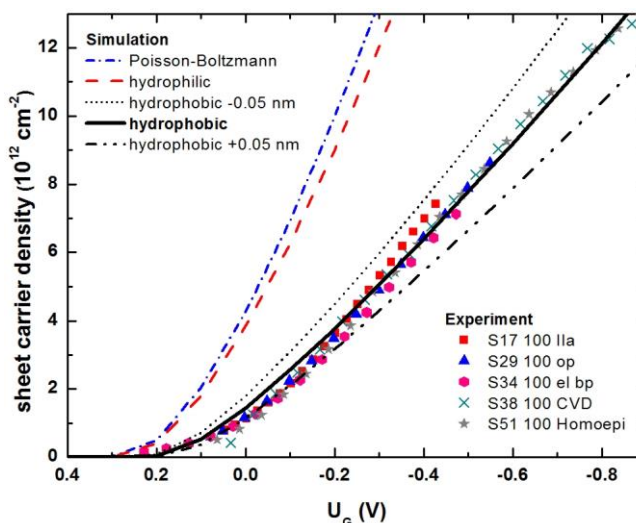


Fig. 2: Comparison of the experimentally obtained carrier concentrations (symbols) for different gate potentials U_G with our calculations. The extended Poisson–Boltzmann model for the hydrophobic interface (black solid line) shows excellent agreement whereas a hydrophilic interface (red dashed line) and the conventional Poisson–Boltzmann model (blue dash-dotted line) overestimate the density.