MODELING OF SEMICONDUCTOR / ELECTROLYTE NANOSTRUCTURES WITH NEXTNANO^3

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ABSTRACT

The quickly progressing technology of low-dimensional semiconductor nanostructures requires and depends on reliable predictive theoretical methods for systematically improving, designing and understanding the electronic and optical properties of such structures. The situation becomes even more complicated if these nanostructures are combined with biomaterials to form bio-sensors [1]. These sensors are gaining importance due to their large potential in commercial applications, like pH, protein, virus or DNA sensors (bio-chips). Ion-selective field effect transistors (ISFETs) usually contain biomaterials in an electrolyte and consist of a two-dimensional electron (or hole) gas (2DEG) in the semiconductor region where a source-drain voltage is applied in the 2DEG plane. The measured source-drain current depends on the electron density in the 2DEG. The goal is to influence the electron density in the 2DEG in a reproducible manner through changes in the electrostatic potential which are caused by the charge distribution inside the electrolyte and in the vicinity of the interface between the semiconductor and the electrolyte, i.e. the electrolyte acts through this field effect as a gate. Several variations of this concept are possible, e.g. instead of having a 2DEG one could use a nanowire with quantum confinement in two directions, and thus enhance the sensitivity due to the increased surface-to-volume ratio, or one could use an optical device where the electrostatic potential in the electrolyte modifies transition energies in quantum wells, quantum wires or even quantum dots. We will present realistic models of the electrolyte solution, its interaction with the semiconductor device surface, and of the semiconductor device itself.

An electrolyte is an aqueous solution containing dissolved ions (e.g. Na^+, Cl^-) that result from the dissociation of salts. Electrolytes that are used as bio-sensors are usually buffer solutions and therefore resist changes in H_3O^+ and OH^- ion concentrations (and consequently the pH) upon addition of small amounts of acid or base, or upon dilution. The concentrations of the ions that are contained in the buffer depend on the pH and the pK'_a value (dissociation constant) and can be calculated using the well-known Henderson-Hasselbalch equation. In addition, the pK'_a value depends on temperature and on ionic strength in a self-consistent way. For instance, when using a phosphate buffer (PBS), the concentrations of the buffer ions at a particular pH are governed by three different pK'_a values and thus it is extremely difficult to derive the concentrations analytically. However, they can be calculated numerically in an iterative scheme [2]. We extended this scheme to allow the variables pH, pK'_a and ionic strength to vary

with spatial coordinates. Such an approach is necessary for analytes that produce local charge variations in the electrolyte, e.g. a charged molecule that binds to the semiconductor device surface. Furthermore, a local variation of pH is critical for the operation of EnFETs (enzyme field effect transistors) where the enzyme reaction depends on the pH value. The distribution of all ion charges in the electrolyte is governed by the Poisson-Boltzmann equation. Conventionally, this equation is linearized which leads to the Debye-Hückel approximation. However, as we will demonstrate, such a simplification is generally not applicable in real devices and only valid for special and very limited cases. The solution $\phi(\mathbf{x})$ of the Poisson-Boltzmann equation determines the charge density in the electrolyte at position $\mathbf{x}$

$$\rho(\mathbf{x}) = \sum_{i=1}^{n} z_i e c_{i,0} \exp\left(-\frac{z_i e\left(\phi\left(\mathbf{x}\right) - U_{\mathrm{G}}\right)}{k_{\mathrm{B}}T}\right), \tag{1}$$

where z_i is the ion valency, e is the positive elementary charge, $c_{i,0}$ is the bulk concentration of the ion species i and $k_{\mathrm{B}}T$ is the thermal energy of the system at temperature T. The bulk electrolyte potential $\phi(\infty)$ can be adjusted by varying the potential of the reference gate electrode U_{G} that is connected to the electrolyte (Dirichlet boundary condition). $\phi(\mathbf{x})$ is the electrostatic potential that is obtained by solving the nonlinear Poisson-Boltzmann equation in the overall device self-consistently, i.e. both in the electrolyte as well as in the semiconductor region. Interface reactions can be taken into account by the so-called site-binding model for amphoteric oxide surfaces [3, 4] where the adsorption and dissociation of H$^+$ and OH$^-$ ions at the interface between the electrolyte and the oxide lead to interface charge densities which depend on both the electrostatic potential at the interface and the pH of the electrolyte. We have implemented these models into the software package next**nano**^{3} [5]. This enables us to model combined semiconductor-electrolyte systems in one [6, 7], two and three dimensions for arbitrary geometries and material compositions. We present results of one- and two-dimensional simulations of protein, DNA and pH sensors based on different semiconducting materials (silicon, diamond and gallium nitride), as well as optical bio-sensors based on quantum wells. We show how the self-consistent calculations of the charge densities and potential distributions for different ion concentrations in the electrolyte can be used to interpret experimental data and to optimize the sensitivity of these devices, e.g. by modifying the dimensions of the nanowire geometry.

REFERENCES

[1] Y. Cui, Q. Wei, H. Park and C. M. Lieber. "Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species". *Science*, Vol. **293**, 1289–1292, 2001.

[2] R. J. Beynon and J. S. Easterby. *Buffer Solutions: The Basics*, Oxford University Press, 1996.

[3] P. Bergveld. "Development of an ion-sensitive solid-state device for neurophysiological measurements". *IEEE Trans. Biomed. Eng.*, Vol. **17**, 70–71, 1970.

[4] T. W. Healy and L. R. White. "Ionizable surface group models of aqueous interfaces". *Adv. Colloid Interface Sci.*, Vol. **9**, 303–345, 1978.

[5] The next**nano**^{3} software can be obtained from http://www.wsi.tum.de/nextnano3 and http://www.nextnano.de.

[6] M. Bayer, C. Uhl and P. Vogl. "Theoretical study of electrolyte gate AlGaN/GaN field effect transistors". *J. Appl. Phys.*, Vol. **97**, 033703 (1–6), 2005.

[7] S. Birner, C. Uhl, M. Bayer and P. Vogl. "Theoretical model for the detection of charged proteins with a silicon-on-insulator sensor". *J. Phys.: Conf. Ser.*, *in press*.