Numerical and analytical models to investigate the AC high-frequency response of nanoelectrode/SAM/electrolyte capacitive sensing elements

Federico Pittino [a,*], Luca Selmi [a], Frans Widdershoven [b]

[a] DIEGM, Università degli Studi di Udine, Udine, Italy
[b] NXP Semiconductors, Leuven, Belgium

ABSTRACT

We develop theoretical models and numerical simulators to accurately describe the AC signal response of nanoelectrodes to the presence of biomolecules, in order to aid the design of capacitive biosensors. In particular, we first develop an analytical model for the electrolyte response to AC signal stimulation, showing that it is possible to define an AC screening length as in the standard Debye–Hückel theory. We then develop a full-custom numerical simulator for a simple nanoelectrode system, where the AC part is solved in the small-signal approximation, coupled to the DC solution. We validate the solver using the analytical model, and then use it to understand the effect of a dielectric biomolecule on the biosensor admittance.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Since their first appearance [1], capacitive biosensors have attracted increasing interest for label-free detection of various analytes, and the progress of CMOS nanoelectronics is opening new opportunities for integrated biosensors based on biofunctionalized electrodes connected to integrated impedance measurement circuitry [2]. While experimental setups [3,4] and fully integrated prototype realizations [5,6] become more numerous, a need for more accurate modeling and simulation of electronic biosensors at the device level is emerging as well.

Simple one-dimensional DC analytical models of, e.g. ISFETs and EISFETs, have been presented, for instance, in [7,8]. Another analytical model, applied to describe the charge screening around nanowire biosensors, is described in [9]. Poisson–Boltzmann solvers have been employed, for instance, in [10,11]. A general approach, based on the self-consistent solution of the DC Poisson–Nerst–Planck and sometimes Stokes equations in a TCAD-like environment is pursued in [12–14]. Most of the work so far has been devoted to silicon nanowire biosensors. To our knowledge, however, at present there has been little work on frequency-domain modeling and simulation of biosensors. In particular, there seems to be limited understanding of high-frequency biosensors (up to 1 GHz), which are starting to become of increasing interest, also in the scope of being able to overcome the limitations due to the electrolyte screening [6,15].

In this paper, we significantly expand our previous work on high-frequency electronic biosensors reported in [16] by extending

the model to AC diffusion currents and steric effects in electrolytes of arbitrary composition. An analytical one-dimensional solution is also derived and used to validate the 2D numerical model.

2. Materials and models

The system considered in this study is the same as reported in [16], and is shown in Fig. 1. Two ideally polarizable flat and circular metallic electrodes delimit a simulation domain with rotational symmetry around the z-axis. On the bottom electrode surface a dielectric self-assembled monolayer (SAM) may be present, which is supposed to be flat, homogeneous, with thickness h_{SAM} and dielectric constant ε_{SAM}. The SAM increases the selectivity of the electrode in capturing target biomolecules. A spherical or ellipsoidal dielectric biomolecule, centered on the z-axis, is optionally inserted in the electrolyte. Both surface and bulk charges can be specified for the SAM and the biomolecule.

DC calculation. The calculation of the DC electrostatic potential has been described in [16] and is summarized here for the sake of a self-contained treatment of the AC problem as well: we assume no electrochemical reactions, hence, zero DC current at the electrodes. Thus the concentration of the mth ionic species (n_{0m}, in m^{-3}) with signed valence Z_m follows an equilibrium Boltzmann distribution:

$$n_{0m} = n_{0m}^{\infty} \exp\left(-\frac{Z_m q (V_0 - V_{ref})}{k_B T}\right) \quad (1)$$

where V_{ref} is the reference potential in the bulk electrolyte and n_{0m}^{∞} the bulk concentration; as usual, q is the absolute value of the elementary charge, k_B Boltzmann's constant and T the absolute temperature. It has to be noted that defining a reference potential is

* Corresponding author.
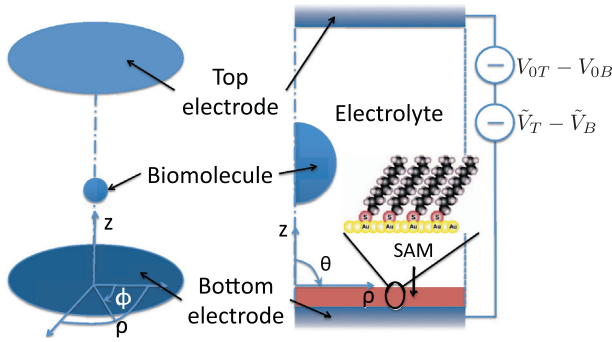   E-mail address: federico.pittino@uniud.it (F. Pittino).

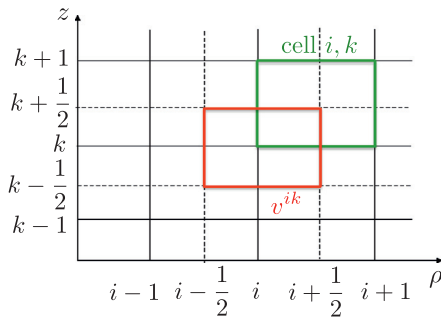Fig. 1. Schematic representation of the system under study.

Fig. 2. Sketch of the mesh in the ρ–z plane, showing the volumes v^{jk} and the cells (i,k) where permittivity $\varepsilon^{i,k}$ is defined.

equivalent to placing an additional reference electrode in the bulk of the electrolyte, sufficiently far from the electrodes. This is possible because the geometric dimensions of the systems we consider are sufficiently large, so that it is always allowed to define a bulk region.

By exploiting the rotational symmetry, a non-uniform grid of rectangular cells with homogeneous dielectric constant $\varepsilon^{i,k}$ (green[1] in Fig. 2) is established in the ρ–z plane. Gauss's law

$$\oint_{\partial v^{ik}} \varepsilon \overrightarrow{E}_0 \cdot \hat{n} \, dS = Q_0(v^{ik}) \qquad (2)$$

with $\overrightarrow{E}_0 = -\nabla V_0$ is solved in the domain following a finite difference scheme [17]. In particular, Eq. (2) is applied to each cell volume v^{ik} around point (i,k). The border of v^{ik} (∂v^{ik}, the red contour in Fig. 2) is determined by the position of the interleaved-grid points $(i \pm 1/2, k \pm 1/2)$. The concentrations (and so the charge) are discretized according to the finite volume method, following the approach presented in [18] and assuming them constant in the dual volume v^{ik}. Because of rotational symmetry around the z-axis, the azimutal components of $\overrightarrow{E}_0$ are zero.

Special care is necessary when applying Eq. (2) to the boundary cells: we use Dirichlet conditions on the electrodes and Neumann conditions (zero outer flux) on the other boundaries. Moreover, second order corrections have been introduced to reduce the discretization error in those cells that are crossed by the boundaries between the biomolecule and the electrolyte.

AC calculation. The equations for the time-dependent problem are the Nernst–Planck equations (known as drift–diffusion equations in semiconductor physics):

$$\frac{\partial n_m}{\partial t} = -\frac{1}{Z_m q} \nabla \cdot \overrightarrow{J}_m \qquad (3)$$

$$\overrightarrow{J}_m = -Z_m q (Z_m q \mu_m n_m \nabla V + D_m \nabla n_m) \qquad (4)$$

where μ_m is the mobility of the mth ionic species (in (m/N s)) and D_m its diffusivity (in (m²/s)). The ionic current expression we use looks different from the one normally employed in electrochemistry and semiconductor physics (see for instance [19]) because we have chosen to define the ion mobility, consistently with classical physics, as the ratio between the ion velocity and the force applied to it. Following this definition Einstein's relation is expressed as $D_m = \mu_m k_B T$.[2]

Working in the frequency domain, we can write $n_m = n_{0m} + \Re(\tilde{n}_m \exp(j\omega t))$ and $V = V_0 + \Re(\widetilde{V} \exp(j\omega t))$ where j is the imaginary unit. Using the small signal approximation on the Nernst–Planck equation and integrating it over the volume v^{jk} (Fig. 2), we obtain:

$$j\omega \tilde{n}_m v^{ik} = \int_{\partial v^{ik}} (Z_m q \mu_m (n_{0m} \nabla \widetilde{V} + \tilde{n}_m \nabla V_0) + D_m \nabla \tilde{n}_m) \cdot \hat{n} \, dS. \qquad (5)$$

Denoting N the number of ion species, the system (5) represents N equations in the $N + 1$ unknown $\tilde{n}_m$ and $\widetilde{V}$. The system of equations is closed via Poisson's equation, which we write in the integral form:

$$-\frac{1}{q} \int_{\partial v^{ik}} \varepsilon \nabla \widetilde{V} \cdot \hat{n} \, dS = v^{ik} \sum_{m=1}^{N} Z_m \tilde{n}_m. \qquad (6)$$

We discretize the equations using a finite difference scheme and the finite volume method following again the approach presented in [18]. We use again mixed Dirichlet/Neumann boundary conditions, imposing no net ionic current flowing out of the domain.

The admittance is finally calculated from the displacement current $\widetilde{J}_D = \frac{\partial D}{\partial t} = j\omega \varepsilon \widetilde{E}$ as the ratio of the total current at the contacts $\widetilde{I}$ and the applied potential $\widetilde{V}$.[3]

Meshing of the domain is especially critical in both DC and AC cases because of the very short Debye length and large interelectrode distance. To cope with the scale change, the mesh spacing near the surfaces is chosen according to the Debye length, while it increases in the bulk regions. To speed up the calculations and obtain solutions of high accuracy we have employed a simple version of Richardson extrapolation, which has been extensively described in [16].

2.1. Electrolyte permittivity

As we will shortly see, to overcome the electrolyte screening it is in principle advantageous to work at very high frequency, in the GHz range. In this range, however, the dependency of the water permittivity on the frequency becomes not negligible. Therefore, to describe the dependency of the water permittivity on the frequency and on the salt concentration, we used a widely known double time constant Debye model [20]:

---

[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

[2] This approach is justified noting that, in semiconductor physics and electrochemistry, there are equations describing relations between phenomena that do not contain charge, like for example Einstein's relation which can be derived from a thermodynamic equilibrium between mechanical force and diffusion on the one hand, and the Boltzmann exponent on the other hand. This means that this family of equations also holds for neutral particles. However, with the semiconductor physics definition of mobility for instance, neutral atoms would have zero mobility, while still reacting to other forces. This dilemma is introduced in semiconductor physics, because it only treats charged particles and the only source of force is the electric field. Therefore, the approach we use gives a broader and more general view on the real physical phenomena.

[3] We point out that the ion currents do not contribute because they are zero at the periphery of the domain. This happens because we assume no electrochemical reactions at the interfaces (therefore no Faradaic currents at the contacts), and therefore the current density through the interfaces and the electrodes consists of displacement current only.