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Modelling of the low-frequency solvent dielectric permittivity in porous silicon nanochannels in the electrical double layer length range

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Electrical double layer (EDL), consists in a shielding layer that is naturally created within the liquid near a charged surface. The thickness of the EDL is given by the characteristic Debye length whole typical value ~1nm depends on the ionic contents in the solvent. The electrokinetic effects in nanochannels depend essentialy on the distribution of charged species in EDL, described by the Poisson-Boltzmann equation those solutions require the solvent dielectric permittivity. A model for solvent low-frequency permittivity profile is proposed, taking into account both the porous silicon (PS) electrode and aqueous solvent properties in the Debye length range.

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1. Introduction

Needs of the modern semiconductor electronics and optoelectronics technologies tend to minimize the size of devices up to nanometer scale. At the same time the their ability to direct formation the spatial structure details is limited only by tenths of micron. Typically PS is obtained in process of etching of positively biased crystalline silicon in hydrofluoric acid solutions (as called anodization process). Depending on the type of starting material and conditions of the anodization process, various forms of PS as sponge-like or wire-like silicon, with different structure and properties were obtained. The size of elements in PS, e.g. radius of pores, vary from nanometers to several microns.

Recent studies showed that the behaviour of PS can be altered in between bioinert, bioactive and resorbable by varying the porosity of the silicon sample. The in-vitro study used simulated body fluid containing ion concentration similar to the human blood and tested the activities of PS sample when exposed to the fluids for prolonged period of time. It was found that high porosity mesoporous layers were completely removed by the simulated body fluids within a day. In contrast, low to medium porosity microporous layers displayed more stable configurations and induced hydroxyapatite growth. Subsequently it was found that hydroxyapatite growth was occurring on PS areas and that silicon itself should be considered for development as a material for widespread in vivo applications [1]. PS may be used a substrate for hydroxyapatite growth either by simple soaking process or laser-liquid-solid interaction process [2].

PS is a redoubtable candidate for use in dynamic new field of nanofluidics. Nanofluidics is defined as the study and application of fluids flow in and around nanometer seized objects with at least one characteristic dimension below 100 nm. Their methods permet using single-molecule modes of molecular manipulation for complex analysis as in micro total analysis systems (µTAS). For exemple, the molecules can be controlled by charge in nanochannels because of their electrostatic interactions with EDL, a shielding layer that is naturally created within the liquid near a charged surface. The thickness of the EDL is given by the characteristic Debye length what grows less with the ionic strength defined by half summ products of concentration with square of charge for all solvent ions (co-ions, counterions, charged molecules). The typical length scale for the Debye length is on the order of 1 nm, depending on the ionic contents in the solvent; thus, the EDL becomes significant for nano-capillaries.

The EDL properties depend on both electrode (pore wall) and solvent nature. The shallow layer of pores is strongly disordered, with various donor and acceptor defects; moreover, the surface of PS is passivated with hydrogenated amorphous silicon, oxide layer SiO_2, also with mono, di- and tri-hydride terminations. By chemical reactions of water with non-bonded oxygens, the PS surface is saturated by polar hydroxyl groups (OH); thus, the pores are hydrophilic and adsorption effects are anticipated. A controlated removal of hydroxyl groups leads to the hydrophobicity of the pores due to absence of polar groups on the surface. The presence of all these defects promotes an high activity of surface by physical and chemical adsorptions of a variety of molecules from organic solvent [3]. It is found that B50 rat hippocampal cells have clear preference for adhesion to PS over untreated surface [4].

The electrokinetic effects in nanochannels depend essentialy on the distribution of charged species in EDL, described by the Poisson-Boltzmann equation those solutions require the solvent dielectric permittivity. In this work we propose a model for solvent low-frequency permittivity profile taking into account both the electrode and solvent properties in the Debye length range.

2. EDL of porous silicon-electrolyte system

The PS devices pick and analyze the results about on an interfacing unknown electrolyte system, coupling the power of detection to the selective and sensitive interaction with electrolyte components. The efficiency of the above mentioned applications is raised by the great specific area of PS that range from $\sim 100 m^2 cm^{-3}$ for macroporous silicon to $\sim 900 m^2 cm^{-3}$ for nanoporous, so that the charged solid-liquid interface parameter is increased importance in nanochannels.

At interface of a semiconductor electrode with an electrolyte, an equilibrium is established through a mechanism of charge transport between the two phases, until the Fermi level ε_F of the semiconductor equals the Redox Fermi level ε_{FR} of the electrolyte [5]. This transport is carried out by electron transfer from the conduction band (for *n*-semiconductor) or by hole transfer from the valence band (for *p*-semiconductor) to the electrolyte. The redistribution of charges at interface results in an electric double-layer with three distinct regions [6], Fig.1: the Space Charge Layer (SCL) consisting in fixed charges in semiconductor, the Helmholtz layer (HL) with fixed charges and the Diffuse Layer (DL) with free charges in electrolyte. A typical value of high charge density and fully ionized electrode surface is σ_s = 0.3 Cm^{-2}, corresponding to one charge per $\sim 0.5 nm^2$.

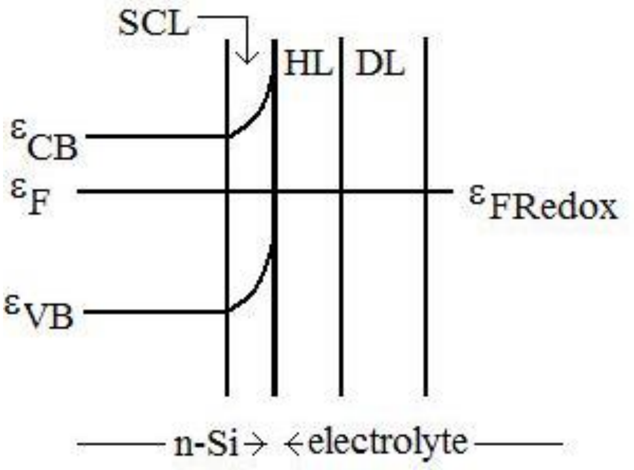

Fig.1. Equilibrium energy levels across an n-Si/electrolyte interface .

The SCL layer consists in fixed charges at semiconductor surface. Sign of charge depends on the semiconductor type *n*- or *p*- and on the relative position of ε_F and ε_{FR}. For exemple, for the *n*-Si/electrolyte interface, if $\varepsilon_F > \varepsilon_{FR}$, the SCL is an inversion layer (positive charged), if $\varepsilon_F < \varepsilon_{FR}$ is an accumulation layer (negative charged), and if $\varepsilon_F = \varepsilon_{FR}$ is no charge transfer. The HL is a bilayer: a) first atomic layer up to inner Helmholtz plane (IH) consists in specifically (nonelectric) adsorbed nonhydrated anions (ions dissoluted from semiconductor surface, that is co-ions) and nonhydrated cations (ions in solution, that is counterions) and polarized water molecules; b) second atomic layer up to outer Helmholtz plane (OH) consists in nonspecifically (electric) adsorbed hydrated cations. All nonhydrated, partially hydrated, hydrated co-ions and counterions from HL are fixed charges, Fig.2.The DL is defined that the region between the HL and the bulk electrolyte, where diffuse free hydrated counterions, hydrated co-ions, water molecules. This layer is characterized by a deviation of ion concentration with respect to the bulk values [7], Fig. 2.

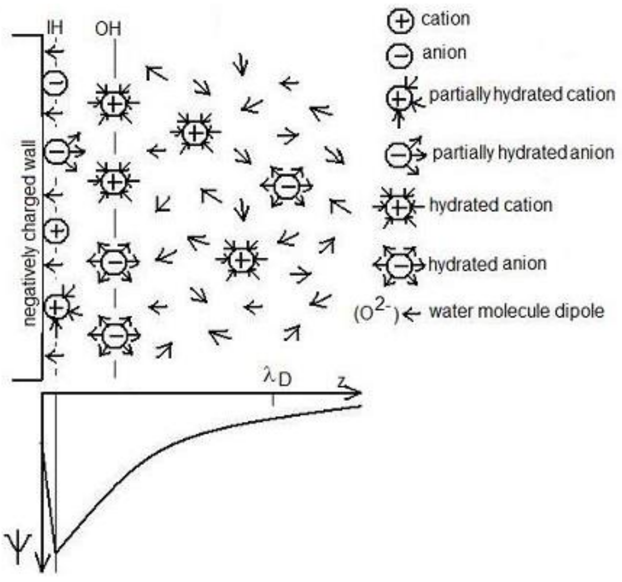

Fig. 2. EDL structure for p-Si (SCL negative charged, $\varepsilon_F < \varepsilon_{FR}$)/aqueous solvent interface. The electrostatic potential and charged atoms in solvent distributions vs the distance z from the wall.

The spatial distribution of the electrostatic potential due to a distribution of charged atoms from DL is shown in Fig.2 and may be described by the complet Poisson-Boltzmann equation [8]

$$\varepsilon_0 \nabla\left[\varepsilon(\vec{r})\nabla\psi(\vec{r})\right] = -\rho(\vec{r}) \qquad (1)$$

where $\rho(\vec{r})$ is the volume charge density of all ions present in the neighborhood of the solid surface, $\varepsilon(\vec{r})$ and ε_0 are the solvent and vacuum permittivity, respectively. All three variables of equation are function of position vector $\vec{r}$. In the Debye-Hückel approximation, e.g. the surface potential is small everywhere in the EDL ($e\psi(z) < k_B T; \psi(z) < 25.7 mV$ at 25^0 C), [7], the complet Poisson-Boltzmann equation is:

$$\nabla^2\psi = \frac{1}{\lambda_D^2}\psi(z) \tag{2}$$

where

$$\lambda_D = \left(\frac{e^2 \sum_i n_i^{\infty} z_i^2}{\varepsilon_0 \varepsilon_r k_B T} \right)^{-\frac{1}{2}} \tag{3}$$

is the Debye length.This value corresponds to the thickness of the EDL that thus depends on the ionic strength of solvent, defined by

$$I_s = \frac{1}{2}\sum_i c_i z_i^2 \tag{4}$$

where c_i, z_i are the bulk solvent molar concentration and the valence of ion i, respectively, and sum refers to all mobile ions from solvent; n_i^{∞} is the bulk solvent (for $\psi = 0$) density of the i ionic species. The EDL permittivity is $\varepsilon_{EDL} = \varepsilon_0 \varepsilon_r(\vec{r})$ and reflects the polarization properties of a complex system consisting from co-ions, counterions, molecules, solvent dipoles, so that $\varepsilon_{EDL} \neq \varepsilon_{puresolvent}$. This result shows that both nature and composition of solvent adjust the thickness of the EDL.

On the other hand, the dielectric properties of the embedding solvent medium affect dramatically the properties of solid electrode. For exemple, in the case of an embedding medium with a large low-frequency dielectric constant, such as a polar solvent, the PS red luminescence shift to green luminescence. Moreover, the red-green switch depend of changing the embedding medium [3].

The surface of fresh PS is almost completely covered by hybride species that SiH, SiH_2, SiH_3, which exhibits a highly hydrophobic character in aquous electrolyte, whereas the storage in ambient air at room temperature causes natural oxidation, giving rise to a passivated surface mainly covered with silanol groups (Si-OH) and showing hydrophilic properties [9]. This fact favours the introduction of the solvent within the pores. The dissolution of the PS surface occurs both in alkaline solution and simulated physiological conditions. If for some biomedical applications material dissolution may even be desirable, others require a stable interface between the pores and an aqueous environment.

The EDL structure and properties depend essentially both on the electrode (pores wall) and the solvent properties and theirs knowledge is the mainly task for each device or application.

3. Contribution of the mobile ions to low-frequency solvent permittivity

Thickness of the EDL is small $(10^{-1} \div 10^2 nm)$ enough to assume that the rest (majority) of the bulk solvent is electro-neutral, but in capillaries on the order even of one micron, the EDL becomes significant. The correct solutions of the Poisson-Boltzmann equation for electrostatic potential of EDL need the knowledge of the spatial dispersion of solvent permittivity.

The dispersive behaviour of a material results in local dispersive constitutive relations, i.e., in frequency–dependent constitutive permittivity and permeability tensors [10]. Spatial dispersion is a nonlocal dispersive behaviour; this results in a constitutive tensors depending on the spatial derivates of the mean fields or, for plane electromagnetic wave, on the wave-vector $\vec{k}$. Specifically, spatial dispersion appears when the higher-order terms in power series of the dimensionless parameter $\frac{a}{\lambda}$ (a is a characteristic microscopic length or the mean free path of the charge carriers, and λ is the wavelength inside the medium), are not neglected. The spatial dispersion appears in addition to the frequency dispersion, but their effects can lead to qualitatively new phenomena, such as the creation of a additional electromagnetic wave.

The EDL contains more ions than solvent bulk having a screening effect of the atom-atom interaction. The dielectric permittivity contribution may be approximated by

$$\varepsilon_{screen}(q) \cong 1 + \frac{\kappa^2}{q^2} \tag{5}$$

where $\kappa = \lambda_D^{-1}$ is an screening length [11] and $q = \frac{k}{\sqrt{\varepsilon(0)}}$ is the wave-vector of field in the medium with the static permittivity $\varepsilon(0)$, [12]. On the other hand, in an ac field, the permittivity is a measure of the conductivity due to the mobile ions motion, so that is active a new contribution,

$$\varepsilon_{conductivity}(\omega) = -i\frac{\sigma}{\omega\varepsilon_0} \tag{6}$$

where σ is the solvent conductivity [13]. The complex dielectric permittivity takes the form $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, where $\varepsilon'(\omega)$ is the relative permittivity, and $\varepsilon''(\omega)$ is the relative loss factor consisting in two contributions: energy losses due to the orientation of molecular dipoles and energy losses due to the conduction of mobile ionic species.

The dielectric analysis technique (DEA) consists in showing the frequency dependence of the relative permittivity $\varepsilon^{'}(\omega)$, of the relative loss factor $\varepsilon^{''}(\omega)$, and of the dissipation factor or loss tangent defined by $tan\,\delta = \dfrac{\varepsilon^{''}(\omega)}{\varepsilon^{'}(\omega)}$. It is also of interest, the Nyquist isotherm diagrams $\varepsilon^{''}(\omega) = f((\varepsilon^{'}(\omega))_{T=const.}$ and also $\varepsilon^{''}(T) = f((\varepsilon^{'}(T))_{\omega=const.}$ [14].

This work proposes a simple model for the permittivity of EDL that a phenomenological parameter with spatial and temporal dispersion. Consequently, the DEA study was carried out.

4. Model

In the long wavelength range of the electromagnetical field, in an anisotropic medium, the dielectric permittivity tensor $\varepsilon_{ij}(\omega,\vec{k})$ connects the Fourrier transforms $D_i(\omega,\vec{k})$ and $E_j(\omega,\vec{k})$ of the $\vec{D}(\vec{r},t)$ and $\vec{E}(\vec{r},t)$ fields by the constitutive relation

$D_i(\omega,\vec{k}) = \varepsilon_{ij}(\omega,\vec{k})E_j(\omega,\vec{k})$, [11]. With usually approximation $\dfrac{\kappa^2}{q^2} \sim \dfrac{\lambda^2\varepsilon(0)}{\lambda_D^2} > 1$ and defining the conductivity relaxation time $\tau_\sigma = \dfrac{\varepsilon_0\varepsilon(0)}{\sigma}$ that determines the rate at which the electric field intensity, E, decays to zero, after their application on a conducting dielectric medium and before dipolar relaxations (that is, $D = const.$), then, the equivalent dielectric permittivity contribution due to mobile ions, may be expressed as:

$$\Delta\varepsilon(\omega,\vec{q}) = \frac{\varepsilon(0)}{\dfrac{\lambda_D^2}{\lambda^2} + i\omega\tau_\sigma} \tag{7}$$

Hypothesis

- the solvent with EDL is an anisotropic continuum medium;
- the wavelength of the field exceeds the thickness of EDL, i.e., $\dfrac{\lambda_D}{\lambda} \le 1$;
- the frequency range of the field is so that the period is before on least dipolar relaxation time, (this is low-frequency range), i.e., $\omega\tau_\sigma \le 1$;
- in this medium, the ionic conductivity depends weakly on frequency, because all the free energy barriers have the same average height.

5. Results

The results of the model show the frequency-dependences $\varepsilon'(log\,\omega\tau_\sigma), \varepsilon''(log\,\omega\tau_\sigma)$ and $\varepsilon''(\varepsilon')_T$, where $\varepsilon', \varepsilon''$ are the real and imaginary part, respectively, from (7), having the $\dfrac{\lambda_D}{\lambda}$ ratio as parameter. In Fig. 3,4,5 the symbols have following significance: −○− $\dfrac{\lambda_D}{\lambda} = 1$; −●− $\dfrac{\lambda_D}{\lambda} = 0.1$; −Δ− $\dfrac{\lambda_D}{\lambda} = 0.01$; −▼− $\dfrac{\lambda_D}{\lambda} = 0.001$.

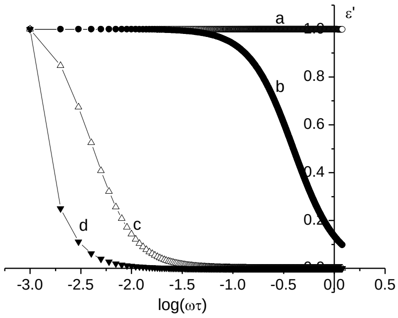

Fig. 3. The dependences $\varepsilon'(log\,\omega\tau_\sigma)$. *The values are normalized at* $\varepsilon^{'}_{max}$.

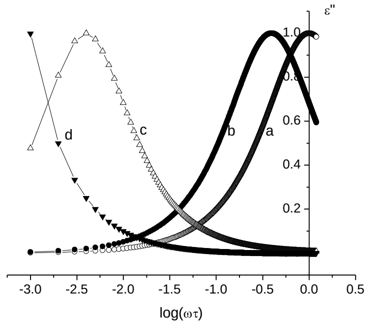

Fig. 4. The dependences $\varepsilon''(log\,\omega\tau_\sigma)$. *The values are normalized at* $\varepsilon^{''}_{max}$.

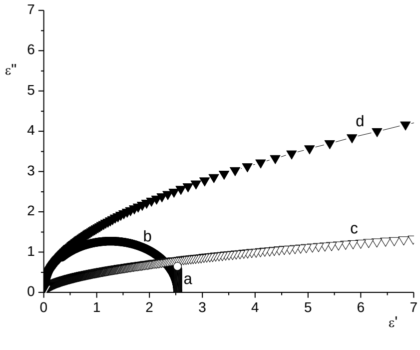

Fig. 5. Isothermal Nyquist diagrams $\varepsilon''(\omega\tau_\sigma) = f(\varepsilon'(\omega\tau_\sigma))_T$.

The dielectric analysis follow the increase of the ionic strength (that is, decrease of the λ_D).

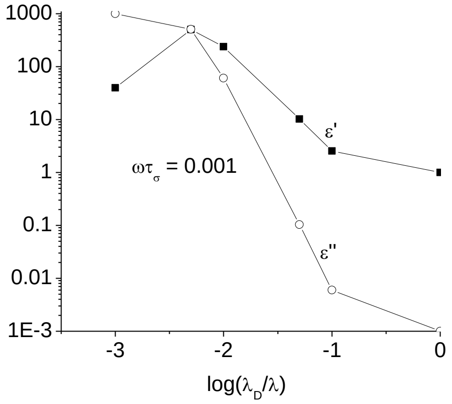

Fig .6. Dependences of $\varepsilon'(\omega\tau_\sigma)$ *and* $\varepsilon''(\omega\tau_\sigma)$ *on* $\frac{\lambda_D}{\lambda}$*, for* $\omega\tau_\sigma = 10^{-3}$.

The analysis shows following features: *i*) the relative permittivity $\varepsilon'(\omega)$ increases then λ_D decreases up to value $\frac{\lambda_D}{\lambda} = \omega\tau_\sigma$, Fig. 6, and the inflexion point moves to low frequencies, Fig. 3; *ii*) the relative loss factor $\varepsilon''(\omega)$ increases then λ_D decreases, Fig. 6, and ε''_{max} moves to low frequencies, Fig. 4; *iii*) the form of the $\varepsilon''(\omega) = f(\varepsilon'(\omega))$ diagrams changes from a vertical line (a), to any deformated semicircle (b,c,d) having the angle to real axis below $\frac{\pi}{2}$, (Fig. 5). This behaviour denotes that the EDL is not an ideal capacitor, but also is not a dissipative region, depending both on the EDL thickness and the frequency range of the applied field [7]. The composition of the EDL (by thickness λ_D) determines essentially the dielectric response of the interface system. Compared with experimental results, the dielectric profile of this higher length scales model can provide a more complete description of the solvent properties for a given electrode.

6. Conclusions

EDL is a free and bonded charge region at the solid-electrolyte interface. His composition that depends both on the nature and structure of solid and solvent, make very valuable to be studied by DEA. The influence of the mobile charges from EDL on the low-frequency permittivity may be analyzed in the frame of temporal and spatial dielectric dispersion theory. Both $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ components of permittivity decrease then λ_D decreases. The proposed model provides the dielectric permittivity profile as an easy abordable way for the characterization of the low-frequency properties of solvent for a given electrode surface.

References

[1] L. T. Canham, Advanced Materials **7**(12), 1033 (1995).
[2] L. Pramatarova, E. Pecheva Dimova-Malinovska, R. Pramatarova, U. Bismayer, T. Petrov N. Minkovskis, Vacuum **76**, 135 (2004).
[3] A. G. Cullis, L. T. Canham, P. D. J. Calcott, J. Appl. Phys. **82**(3), 909 (1997).
[4] A. V. Sapelkin. S. C. Bayliss, B. Unal, A. Charalambou, Biomaterial **27**, 842 (2005).
[5] A. J. Bard, L. R. Fanlkner, Electrochemical methods: Fundamentals and applications, John Wiley & Sons, New York, 2000.
[6] R. B. Schoch, P. Renaud, Appl. Phys. Lett. **86**, 253111 (2005).
[7] R. B. Schoch, J. Han, P. Renaud, Rev. of Mod. Phys. **80**, 839 (2008).
[8] J. Aun Ng, T. Vora, V. Krishnamurthy, S.-H. Chung, Eur Biophys. J. **37**, 213 (2008).
[9] V. Demontis, Porous Silicon Applications in biotechnology, Tesi di Dottorato, Universita Degli Studi di Cagliari, 2006.
[10] V. M. Agranovich, Y. N. Gartstein, Physics-Uspekhi **49**(10), 1029 (2006).
[11] A. O. E. Animalu, Intermediate quantum theory of crystalline solids, Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1977.
[12] A. S. Davîdov, Teoria Corpului Solid, Editura Stiintifica si Enciclopedica, 1982.
[13] M. Agrawal, Optical Modeling of Nano-Structured Materials and Devices, Electrical Engineering, Stanford University, 2009.
[14] L. Núñez, S. Gómez-Barreiro, C. A. Gracia_Fernández, M. R. Núñez, Polymer **45**, 1167 (2004).

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