

**TOWARD THE PHYSICAL BASIS OF COMPLEX SYSTEMS:
DIELECTRIC ANALYSIS OF POROUS SILICON
NANOCHANNELS IN THE ELECTRICAL DOUBLE LAYER
LENGTH RANGE**

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ABSTRACT. Dielectric analysis (DEA) shows changes in the properties of a materials as a response to the application on it of a time dependent electric field. Dielectric measurements are extremely sensitive to small changes in materials properties, that molecular relaxation, dipole changes, local motions that involve the reorientation of dipoles, and so can be observed by DEA. 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 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 that nanochannels. The electrokinetic effects in the nanochannels depend essentially 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 and a DEA profile taking into account both the porous silicon electrode and aqueous solvent properties in the Debye length range.

KEYWORDS: *dielectric analysis, nanochannels, electrical double layer, ionic strength, low-frequency permittivity*

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1. INTRODUCTION

Porous silicon studies showed that the behaviour of porous silicon can be altered in between 'bio-inert', '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 porous silicon 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 porous silicon areas and that silicon itself should be considered for development as a material for widespread in vivo applications [1]. Porous silicon may be used a substrate for hydroxyapatite growth either by simple soaking process or laser-liquid-solid interaction process [2].

Porous silicon is a redoubtable candidat 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 (TAS). For exemple, the molecules can be controlled by charge in nanochannels because of their electrostatic interactions with the electrical double layer (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 Si, oxide layer SiO₂, also with mono, di- and tri-hydride terminations. By chemical reactions of water with non-bonded oxygens, the porous silicon surface is saturated by polar hydroxyl groups (OH); thus, the pores are hydrophilic and adsorption effects are anticipated. A controlled 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 porous silicon over untreated surface [4]. The electrokinetic effects depend essentially 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 and a DEA profile taking into account both the electrode and solvent properties in the Debye length range.

2. EDL OF POROUS SILICON-ELECTROLYTE SYSTEM

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]: 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 $\sigma_s = 0.3Cm^{-2}$, corresponding to one charge per $\sim 0.5nm^2$.

The HL is a bilayer: a) first atomic layer up to inner Helmholtz plane (IH) consists in specifically (nonelectric) adsorbed nonhydrated anions (ions dissolved 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.1.

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.1. The spatial distribution of the electrostatic potential due to a distribution of charged atoms from DL may be described by the complet Poisson-Boltzmann equation [8];

$$\epsilon_0 \nabla [\epsilon(\vec{r}) \nabla \psi(\vec{r})] = -\rho(\vec{r}) \quad (1)$$

where $\rho(\vec{r})$ is the volume charge density of all ions present in the neighborhood of the solid surface, $\epsilon(\vec{r}), \epsilon_0$ is the solvent, vacuum permittivity, respectively. All three variables of equation are function of position vector $\vec{r}$. In the Debye-Hückel approximation, [7], the complet Poisson-Boltzmann equation is:

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

where

$$\lambda_D = \left(\frac{e^2 \sum_i n_i^\infty z_i^2}{\epsilon_0 \epsilon_r k_B T} \right)^{-\frac{1}{2}} \quad (3)$$

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

$$I_s = \frac{1}{2} \sum_i c_i z_i^2 \quad (4)$$

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 ($\psi = 0$) density of the i ionic species. The EDL permittivity is $\epsilon_{EDL} = \epsilon_0 \epsilon_r(\vec{r})$ reflects the polarization properties of a complex system consisting from co-ions, counterions, molecules, solvent dipoles, so that $\epsilon_{EDL} \neq \epsilon_{puresolvent}$. 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 silicium porous 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 hybrid species that SiH, SiH_2, SiH_3 , which exhibits a highly hydrophobic character in aqueous 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.

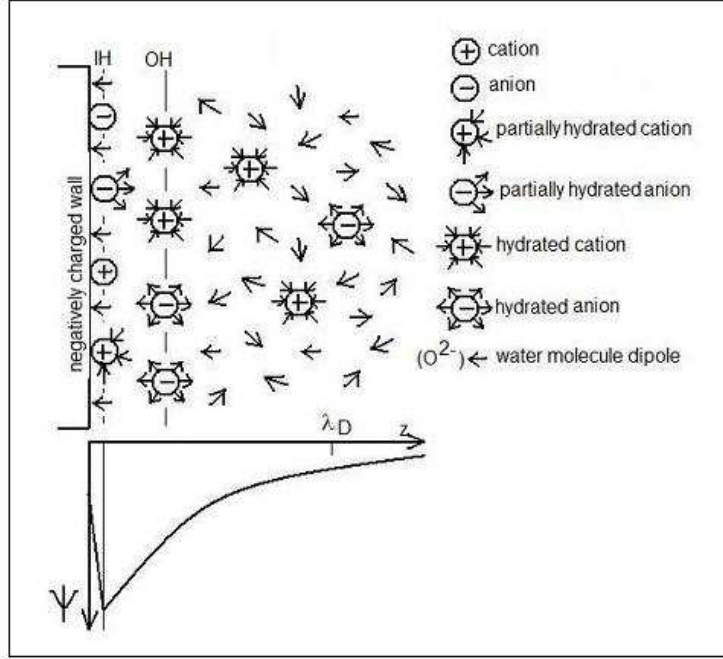


Figure 1: EDL structure for p-Si (SCL negative charged, $\epsilon_F < \epsilon_{FR}$)/aqueous solvent interface. The electrostatic potential and charged atoms in solvent distributions vs the distance z from the wall.

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 [10]. Spatial dispersion is a nonlocal dispersive behaviour; this results in a constitutive tensors depending on the spatial derivatives of the mean fields or, for plane electromagnetic wave, on the wave-vector $\vec{k}$ [10]. 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

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

where $\kappa = (\lambda_D)^{-1}$ is an screening length [11] and $q = \frac{k}{\sqrt{\epsilon(0)}}$ is the wave-vector of field in the medium with the static permittivity $\epsilon(0)$, [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,

$$\epsilon_{conductivity}(\omega) = -i \frac{\sigma}{\omega \epsilon_0} \quad (6)$$

where σ is the solvent conductivity [13]. The complex dielectric permittivity has form $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, where $\epsilon'(\omega)$ is the relative permittivity, and $\epsilon''(\omega)$ 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 consists in showing the frequency dependence of the relative permittivity $\epsilon'(\omega)$, of the relative loss factor $\epsilon''(\omega)$ and of the dissipation factor or loss tangent defined by $\tan \delta = \frac{\epsilon''(\omega)}{\epsilon'(\omega)}$. It is also of interest, the Nyquist diagrams $\epsilon''(\omega) = f(\epsilon'(\omega))_{T=const.}$ and also $\epsilon''(T) = f(\epsilon'(T))_{\omega=const.}$ [14]. This work proposes a simple model for the permittivity of EDL that a phenomenological parameter with spatial and temporal dispersion. Contribution of the mobile ions to low-frequency solvent permittivity is taken into account and, consequently, the DEA study is made. Using the conductivity relaxation time $\tau_\sigma = \frac{\epsilon_0 \epsilon(\omega)}{\sigma}$, 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 solvent mobile ions, may be expressed

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

with hypothesis: i) the wavelength of the field exceeds the thickness of EDL, i.e., $\frac{\lambda_D}{\lambda} \leq 1$; ii) 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., $\omega\tau_\sigma \leq 1$; iii) the ionic conductivity depends weakly on frequency, because all the free energy barriers have the same average height.

3.RESULTS

The results of the model are shown that the frequency-dependences $\epsilon'(\log(\omega\tau_\sigma))$ in Fig.2, $\epsilon''(\log(\omega\tau_\sigma))$ in Fig.3 and $\epsilon''(\epsilon')_T$ in Fig.4, where ϵ' , ϵ'' are the real and imaginary part, respectively, from (7), having the $\frac{\lambda_D}{\lambda}$ ratio as parameter.

In Fig.2, Fig.3, Fig.4 the symbols have following significance: $-\circ-$ for $\frac{\lambda_D}{\lambda} = 1$; $-\bullet-$ for $\frac{\lambda_D}{\lambda} = 0.1$; $-\triangle-$ for $\frac{\lambda_D}{\lambda} = 0.01$; $-\nabla-$ for $\frac{\lambda_D}{\lambda} = 0.001$.

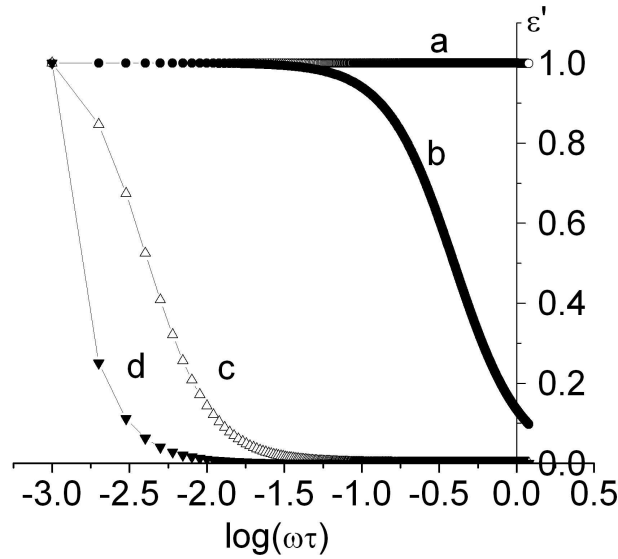


Figure 2: The dependencies $\epsilon'(\log \omega\tau_\sigma)$. The values are normalized at ϵ'_{max}

The dielectric analysis follow the increase of the ionic strength (that is, decrease of the λ_D). Both $\epsilon'(\omega)$ and $\epsilon''(\omega)$ increase then λ_D decrease, and

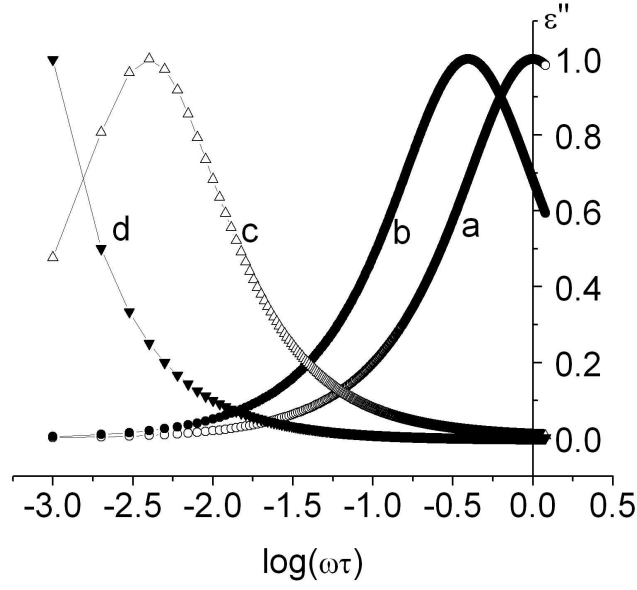


Figure 3: The dependencies $\epsilon''(\log \omega \tau_\sigma)$. The values are normalized at ϵ''_{max}

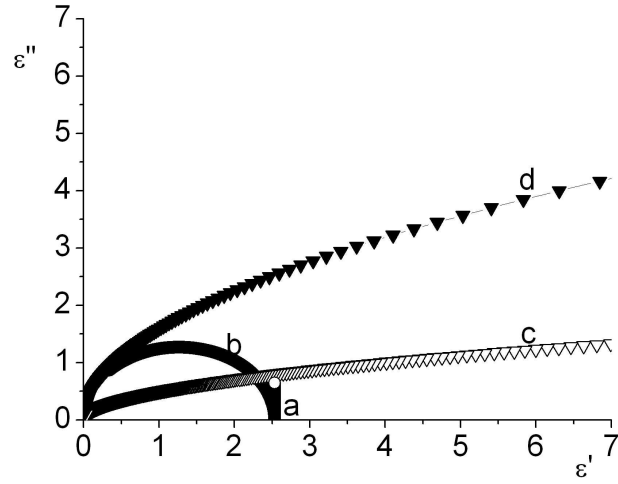


Figure 4: Nyquist diagrams $\epsilon''(\omega \tau_\sigma) = f(\epsilon'(\omega \tau_\sigma))_T$

ϵ''_{max} moves to low frequencies, Fig.3. The conductivity relaxation occurs at lowing frequencies. The form of the $\epsilon''(\omega) = f(\epsilon'(\omega))$ diagrams changes from a vertical line (a), to any deformed semicircles (b, c, d) having the angle to real axis below $\frac{\pi}{2}$, Fig.4. This behaviour denotes that the EDL is not an ideally 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 (by thickness) of the EDL 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.

4.CONCLUSIONS

EDL is a free and bonded charge region at the solid-electrolyte interface. Their 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 $\epsilon'(\omega)$ and $\epsilon''(\omega)$ components of permittivity decrease then λ_D decrease. The proposed model coupled with DEA technique provide the dielectric permittivity profile as an easy affordable way for the characterization the low-frequency properties of solvent for a given electrode surface.

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