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Low-frequency electrical properties of porous silicon

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Silicon is the most commonly used semiconductor material for micro and nanodevices that can be build up on porous silicon. Such devices has a different response for different type of the molecule bounded to the surface of silicon, i.e. polar, positively or negatively charged molecules. As that others physical properties, e.g., luminescence properties, the surface of PS has an essential role in low-frequency (diffusional regime) electrical properties. Impedance spectroscopy results show that the behavior of the free pore surface is similar to EDL (Electrical Double Layer) of electrode-solvent interface; that is cannot by considered as perfectly polarized because the motion of electric charge is possible. But the surface of pore can be partially and selectively polarized. This paper brings information about the electrical behavior of the free surface of porous silicon. Results were obtained from processing the experimental components of the impedance measured in ac electric field on low frequency.

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1. Introduction

It is well known that the nano and microporos systems, with characteristic dimensions below 100 nm, have a high surface-to volume ratio, leading to new physical phenomena when interacts with fluids. Such a situation is not observed at macrofluidic size scales.

A dynamic new field in technology, biology and medicine, is that of the micro total analysis system (μTAS) [1]. This system aims to integrate all steps of biochemical analysis on one microchip by unique modes of biomolecular manipulation [2]. For example, molecules can be controlled by charge in nanochannels because of their electrostatic interactions with the electrical double layer (EDL). This shielding layer is naturally created within the fluid near a charged surface. Moreover, size-based filtration and sieving can be achieved because the length scales of biomolecules and synthetic nanometer-sized objects are similar.

Silicon as porous silicon (PS) is the most commonly used semiconductor nanowire material. A nanowire is an one-dimensional nanostructures that show detectable electrical changes upon interactions with molecules. A device based on silicon nanowire can be build up on porous silicon. The effect is related to their large surface-to volume ratio. Such device has a different response for different type of the molecule bounded to the surface of silicon, i.e. polar, positively or negatively charged molecules.

Silicon is the most commonly used semiconductor nanowire material. A nanowire is an one-dimensional nanostructure that show sdetectable electrical changes upon interactions with molecules. A device based on silicon nanowire can be build up on porous silicon. The effect of appearance of electric charge is amplified because of large surface-to volume ratio of porous silicon. In order to extract exact information about a studied molecule is essential to find a good model for EDL layer. In a given fluid, the structure of EDL layer determines the kinetic of the molecule [14]. Accuracy in extracting and evaluating kinetic parameters ensures the level of the minimum concentration at which a given type of molecule is detected.

Electrochemical Impedance Spectroscopy (EIS) is the most appropriate method for investigating of EDL layer. [3,4]. In EIS techniques the measurements are performed using a small ac amplitude ($\sim 10\,mV$) on a relatively low frequency range, $\left(0.01 \div 10^5\,Hz\right)$. The main characteristics of EDL obtained by this method are the resistance of the electric charge transfer R_t and the value of the electric charge accumulated in the layer C_{EDL}.

This paper brings information about the electrical behavior of the free surface of porous silicon. Results were obtained from processing the experimental components of the impedance measured in ac electric field at low frequencies.

2. Experimental

2.1 Material and method

The PS studied samples have been obtained on silicon wafer in an anodisation set-up without supplementary drayed and protected post-anodisation treatments. Both conductance $G(\omega)$ and capacitance $C(\omega)$ have been measured with an HP impedance-meter, in the $\left(10^3 \div 10^7\right)Hz$ frequency range. Experimental data were processed and interpreted, in two ways:

1) by drawing Nyquist chart $Z''(Z')$. The method consists in analysis and highlighting of the changes in the shape of chart in the considered frequency range in connection with: a) the accumulation and distribution of electrical charge on the pores surface, and b) the relaxation of these configuration during the inactive semi-period of the applied ac field. Considerations are made on the basis of a model for the equivalent electrical circuit of sample;

2) converting the experimental results on the impedance in order to obtain the real part of conductivity $\sigma'(\omega)$ and the real part of permittivity $\varepsilon'(\omega)$. Analysis of dispersion of these quantities provides information about the kinetic mechanisms of polarization of the surface and about the mechanisms of electric charge dynamic in the range of low-frequency ac field.

2.2 Nyquist diagram of the electrical impedance

Nyquist diagram of the electrical impedance of a material system is the dependence $Z''(Z')$, where Z'' and Z' are respectively, the storage and the dissipative component of the impedance Z . The Nyquist diagram of the impedance of the equivalent electrical circuit of the EDL layer is a semicircle with a diameter R_t and an angular frequency at the apex equal to $\left(1/\left(R_t \cdot C_{EDL}\right)\right)$ Fig.1 shows a typical diagram for PS in the considered frequency range.

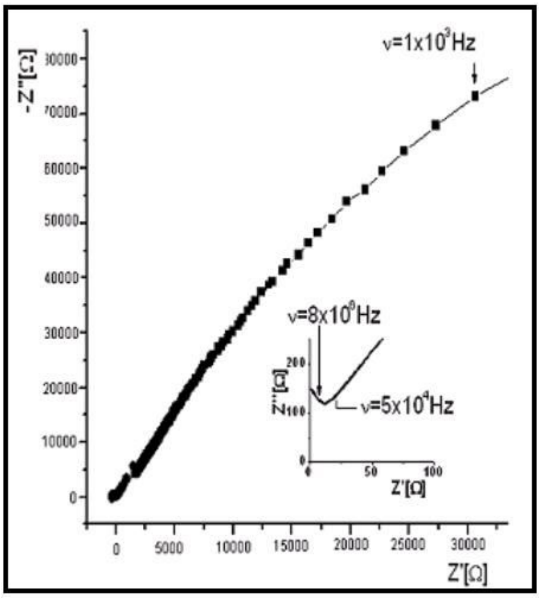

Fig. 1. Nyquist diagram of the impedance.

Analysis of the diagram shows two particular features:

-storage properties (by polarization) are different for high and low frequencies (relative to the frequency range of measurement);

-in the low frequencies range, the chart strongly deviate from the semicircle shape with the center on the real axis, that is characteristic for the dissipation in the situation of Debye type mechanisms of relaxation [5], (Fig. 1, inset)).

2.3 Complex permittivity

The dispersive properties in the considered frequency range may be expressed in the complex permittivity terms

$$\varepsilon_p^* = \varepsilon' - i\frac{\sigma'(\omega) - \sigma_0}{\varepsilon_0 \cdot \omega} = \varepsilon' - i\left[\varepsilon'' - \frac{\sigma_0}{\varepsilon_0 \cdot \omega}\right] \tag{1}$$

Dispersion of ε_p^* must be attributed to other contribution to the frequency dependence of ε^*, other than the simple $\sigma_0/(\varepsilon_0 \cdot \omega)$ term.

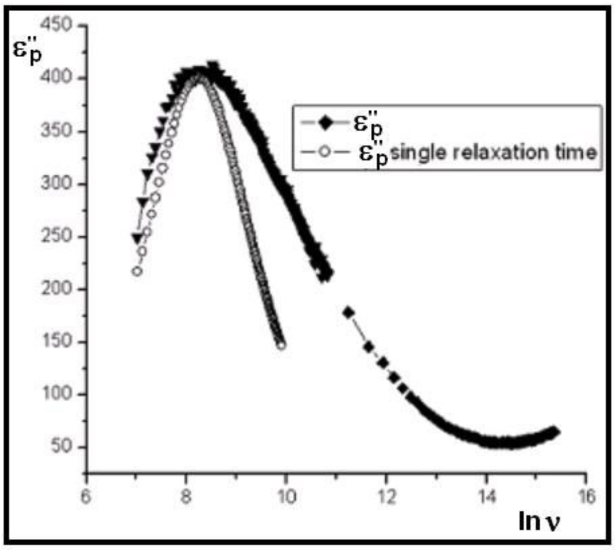

Fig. 2. The experimental dependence $\varepsilon_p''(\omega)$.

Fig. 2 shows the dependence $\varepsilon_p''(\omega)$ and , for comparison, the dependence $\varepsilon''(\omega)$ for a single Debye relaxation time case. The plot of the dependence $\varepsilon_p''(\omega) = f(\ln\omega)$ shows a maximum larger than the single Debye relaxation time plot on both sides of the maximum frequency, but asymmetric and more bended toward the high frequency side of the maximum.

3. Discussion

In the considered frequency range, the dispersive properties owe to the relaxation of electrical free charge accumulated on the surface of pores during the semi-period corresponding to reverse ac electric field [6]. In the expression of the electrical impedance, the capacity C must express storage of charge on the surface of pores, so that C is the equivalent capacity of EDL layer. Depending on the nature of the surface, in the EDL layer a part of the electric charge is bounded, and another part of the electric charge is polarized.

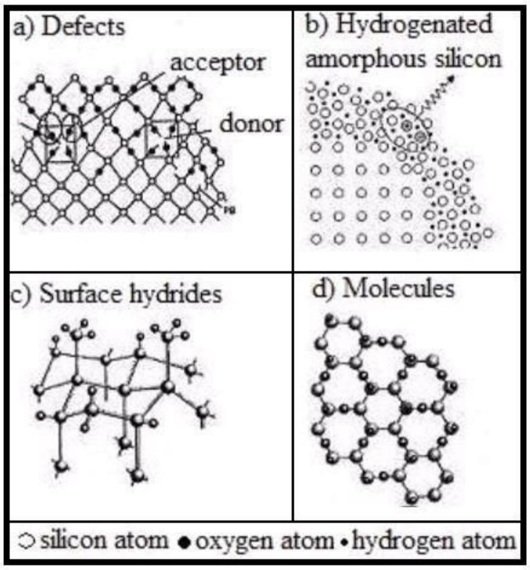

Fig. 3. Defects on the PS surface.

The shallow layer of the PS obtained from crystalline silicon is strongly disordered, as shown in Fig. 3, with various donor and acceptor defects a). The surface of PS is passivated with hydrogenated amorphous Si b), surface passivated with mono, di- and tri-hydride terminations c). The presence of all these defects promotes a high activity of surface by physical and chemical adsorption of a variety of molecules d) passivation by molecules of organic solvent, organometallics, metal salts, aqueous bases and specific gaseous molecules [7].

In the free atmosphere (moist air), the Si atoms having free valences can make bonds with the hydroxyl OH^- or O^{2-} ions [8] and thus they can trap electrons. In the neighborhood of donor states, the free electric charge is polarized .

The dipole molecules located in the neighborhood of the surface of pore induces a supplementary polarization of the surface and consequently an increasing static permittivity of material. The free surface of the pore cannot by considered as perfectly polarized because the motion of electric charge is possible. Nevertheless the surface of pore can be partially polarized.

The surface of pores, a passive complex electrical system, comprises both elements that dissipate the energy (resistor R_t) and elements ensuring the energy storage (capacitor with capacity C_{EDL}). The impedance of the electric system is

$$Z(\omega) = \frac{R_t}{1 + R_t \cdot C_{EDL} \cdot i \cdot \omega} \tag{2}$$

where $R_t \cdot C_{EDL} = \tau$, the relaxation time of the polarization process.

If C_{EDL} is independent on frequency, the Nyquist diagram $Z''(Z')$ is an semicircle centered in $(R_t/2,0)$ on the real axis Z'. It is not the situation from Fig. 1.

This behavior of surface of pores, suggests that the analysis of the electric impedance must be performed using the formalism of constant phase element (CPE). In this case, the storage term of the impedance has the form

$$Z_{CPE}(\omega) = \frac{1}{C_{CPE}(i \cdot \omega)^{n_{CPE}}} \tag{3}$$

where ω is the angular frequency and n_{CPE} is the CPE exponent. C_{CPE} has the numerical value of the admittance $(1/Z)$ at $\omega = 1\,rad/\sec$. The units of C_{CPE} are $S \cdot (\sec)^n$.

For $n_{CPE} = 1$, $C_{CPE} = C$ that is the capacity of EDL layer. In this case all electric charge on the surface is polarized. For $n_{CPE} < 1$, Z_{CPE} expresses the capacitive impedance due only to the polarized (stored) part of electric charge.

The surface layer impedance for PS may be expressed by

$$Z(\omega) = R_\infty + \frac{R_0}{1 + (i \cdot \omega \cdot \tau)^{1-n_{CPE}}} \tag{4}$$

where $R_0 = Z(\omega = 0)$, $R_\infty = R(\omega \to \infty)$. In this case the phase angle of Z is independent of the frequency and has a value $-(90 \times (1 - n_{CPE}))$ degrees.

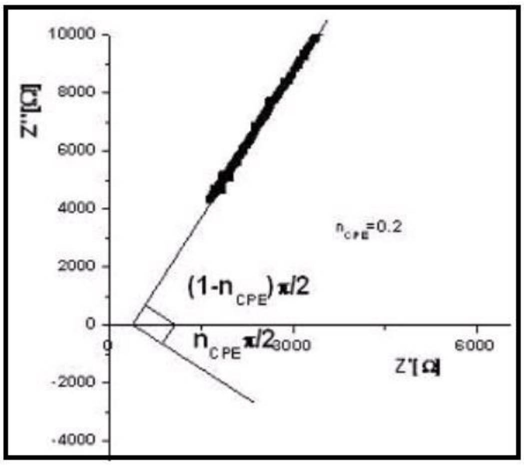

Fig. 4. Low-frequency phase angle of impedance.

From Fig. 4, $n_{CPE} \sim 0.2$ and the phase angle is $-(90 \times 0.8)^\circ = 72^\circ$. This result proves both dissipative and stocking (polarization) behavior of the silicon surface.

In the diffusional regime, the frequency dependence of the complex dielectric function provides a fundamental description of the medium. Then this dependence moves off on the Debye distribution, and can be fit to the Havriliak-Negami (HN) relaxation function [9], defined by

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon(0) - \varepsilon_\infty}{\left[1 + (i \cdot \omega \cdot \tau)^{1-\alpha}\right]^\gamma} \tag{5}$$

where $\varepsilon(0)$ and ε_∞ are static and high frequency permittivity, respectively, τ is the relaxation time. The HN function parameters $0<\alpha<1$ and $0<\gamma<1$ describe the extent of a symmetric continuous distribution around τ, and the broadened skewed distribution, respectively.

It is interesting to compare this dependence with the electric-field-relaxation function, used to describe conductivity relaxation in oxide glasses [10].

$$\varphi(t)=\exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right) \qquad (6)$$

with $\beta=1-\alpha;0<\beta<1$. The exponent $0<\alpha<1$ describes the nonexponentiality of the decay function of field. The exponential relaxation, $\beta=1$, may be achieved with very low cation concentration, so that the approach to single relaxation may be associated with a decrease in cation-cation interactions characterized essentially by independent carriers relaxation in analogy to Debye dipoles [11]. On the other hand, with increase of the nonexponentiality, $\beta<1$, the half-height width Δ of the relaxation function $N^{*}(\omega)$ obtained from the Fourier transform of the derivative of the decay function [12], increases.

The increase of the $\varepsilon_p^{''}(\ln\vartheta)$ plot width to approximately 3.9 vs 2.6 (1.7 vs 1.1 frequency decades) for the Debye relaxation of same relaxation time, may be associated to a rich pores concentration, so that a coupling degree is possible. It is possible also a Debye relaxation time distribution corresponding to that of pore sizes [13].

The asymmetry of the $\varepsilon_p^{''}(\ln\vartheta)$ plot shifted toward the high frequency side of the maximum, may be associated to the dynamic heterogeneity of the material [14]; e.g., the charge is accumulated to long-lived surface states, with time of life greater than the period of the electrical field. These considerations require supplementary proofs deduced from others physical properties.

4. Conclusions

In the case of specific properties, e.g., luminescence properties, the surface of PS has an essential role in low-frequency (diffusional regime) electrical properties. Impedance spectroscopy results show that the behavior of the free pore surface is similar to EDL of electrode-solvent interface; and cannot by considered as perfectly polarized because the motion of the electric charge is possible. Nevertheless the surface of pore can be partially and selectively polarized.

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