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Angular Ellipsometry of Porous Silicon Surface Layers

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An ellipsometric diagnostics of porous silicon samples with different degree of porosity *P* was carried out. The porous silicon samples with degree of porosity of 30 % and 60 % were fabricated on (100) silicon wafers of *p*-type conductivity with a high concentration of boron dopant by etching in solution of HF and ethanol. To characterize the optical properties of porous silicon samples the angular dependences of such ellipsometric parameters as Δ ($\cos\Delta$) and Ψ ($\mathrm{tg}\Psi$) were measured within a wide range of light incidence angles. Due to their angular dependences the principal angle φ_p of light incidence and a value of $\mathrm{tg}\Psi_{min}$ and its angular position were determined. The optical properties of the samples of porous silicon with different degree of porosity after keeping in isopropyl alcohol during one day were also studied. The morphology of the porous silicon surface was investigated by atomic force microscopy. It was found that the ellipsometric parameters are significantly different for these two samples of porous silicon with different degree of porosity *P*, namely the differences in the value of the principal angle of light incidence and the angular position of the $\mathrm{tg}\Psi$ minimum are about 10°. In the framework of the model of the effective medium the obtained result was explained by the presence in porous silicon sample with $P = 60$ % of larger amount of a substance with small refractive index, namely air and silicon oxide formed on the walls of its pores. It was established that treatment of the samples of porous silicon in isopropyl alcohol during one day and subsequent keeping of samples in air atmosphere leads to a decrease in the principal angle of light incidence and refractive index due to porous silicon oxidation.

Keywords: Porous silicon, Optical properties, Oxidation, Film, Ellipsometry.

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1. INTRODUCTION

Silicon as a semiconductor material due to its properties, the perfect technology of mass production and its low cost is still a basic material in modern microelectronics and solar energy. The practical application of silicon may be essentially expanded, creating on its basis the nanostructured and porous media or so-called black silicon [1].

The peculiarities of the morphology of such materials determine their unique electronic properties and make it possible their practical application in microelectronics, optoelectronic and photonic devices, chemical and biosensors, solar cells, drug delivery, etc. [2, 3].

Porous silicon is formed as a layer of different thickness on the surface of the single-crystal silicon in which a huge number of tiny pores are formed as a result of electrochemical etching. The optical properties of these materials differ significantly from those for the single-crystal silicon [4, 5].

In this work, the diagnostics of porous silicon with different degree of porosity by an ellipsometric method was performed and its optical characteristics were compared too. Influence of the treatment of the samples of porous silicon in isopropyl alcohol during one day and subsequent keeping of samples in air atmosphere on ellipsometric parameters was also investigated.

2. SAMPLES AND RESEARCH METHODS

The porous silicon (PS) samples were fabricated by the electrochemical etching of (100) *p*-type silicon wafers with a high concentration of boron dopant (10^{19}-10^{20} cm^{-3}) in a solution of 49 % HF and pure ethanol. The porosity values of the samples (30 and 60 %) were set by the different anodization current densities (10 mA/cm^2 and 150 mA/cm^2, respectively). The PS samples were also treated by isopropyl alcohol during one day. Further, these samples were kept in air atmosphere for certain periods of time.

Optical polarization measurements were carried out using laser ellipsometer LEF-3M-1 at a wavelength of 632.8 nm under atmospheric conditions. For porous silicon samples, ellipsometric parameters such as a phase shift Δ between *p*- and *s*-components of the polarization vector and an azimuth Ψ of the restored linear polarization were measured for two mutually perpendicular directions in own plane of each sample with aim to characterize the optical anisotropy within surface layer of PS samples at variation of the angle φ of light incidence. The angular orientation of the sample in its own plane was conventionally designated by azimuths $\alpha = 0°$ and 90°.

All angular dependences of the ellipsometric parameters $\cos\Delta(\varphi)$ and $\mathrm{tg}\Psi(\varphi)$ of the investigated samples were analyzed and the principal angle φ_p of light incidence ($\cos\Delta = 0$), the angular positions of minimal value of $\mathrm{tg}\Psi_{min}$ and minimal value of $\mathrm{tg}\Psi_{min}$ are obtained from these dependences by method presented in work [6].

The morphology of the PS surface was studied by AFM. The PS samples demonstrate an evidence of regularly shaped pattern on their surfaces (Fig. 1).

The islands oriented in the same direction have shapes which are similar to those influenced by face-centered cubic crystal lattice of the silicon substrate characterized by the Miller indices (100). The morphology of the structured surface is dependent on the sam-

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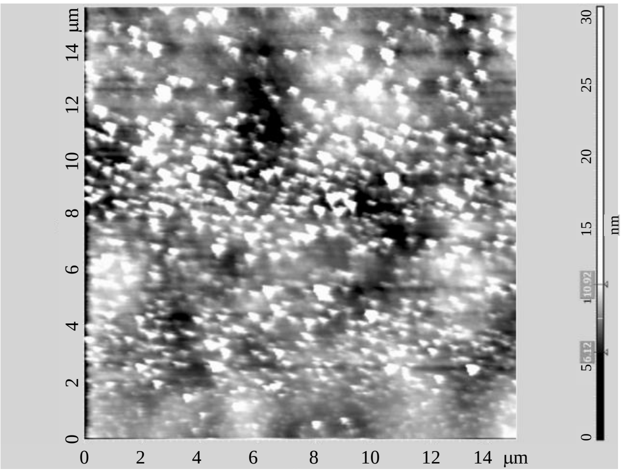
ples fabrication parameters.



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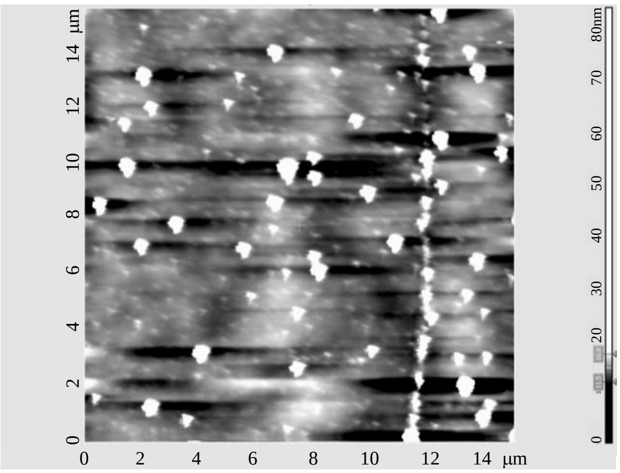


b

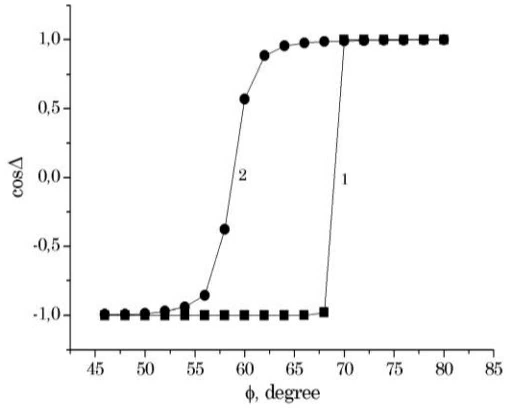
Fig. 1 – AFM images of the surface of PS samples with porosity $P = 30$ % (a) and 60 % (b)

3. RESULTS AND DISCUSSION

The angular dependences of the ellipsometric parameters $\cos\Delta$ and $\mathrm{tg}\,\Psi$ obtained for the two PS samples are shown in Fig. 2.

It was found that angular dependences of both ellipsometric parameters are significantly different for the samples of PS with various degree P of porosity. In particular, the difference in the value of the principal angle of incidence and the angular position of the $\mathrm{tg}\,\Psi$ minimum is about 10°.

For a substance with very small absorption index, the change in ellipsometric parameters is mainly due to changes in the refractive index [7]. The effective refractive indices of the PS samples were obtained in the model of a filmless semi-infinite reflective medium. Significant difference in the value of the refractive indices was obtained for silicon samples with various porosity, namely for the sample with $P = 30$ % it is value of $n = 2.40$, whereas for the sample with $P = 60$ % it is equal to 1.40.



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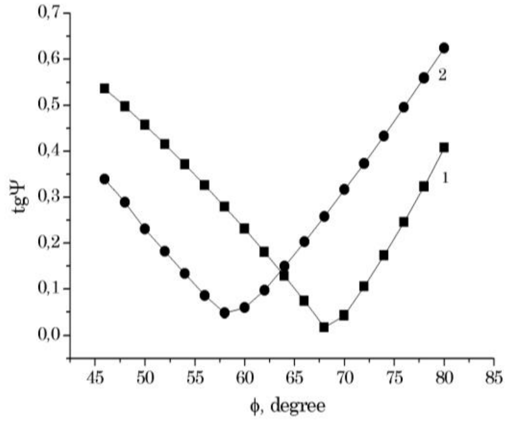

b

Fig. 2 – Dependences of $\cos\Delta(\varphi)$ (a) and $\mathrm{tg}\,\Psi(\varphi)$ (b) for PS samples with $P = 30$ % (1) and $P = 60$ % (2)

In the framework of the model of the effective medium the obtained result may be explained by the presence in Si sample with $P = 60$ % of larger amount of a substance with small refractive index, namely air and silicon oxide formed on the walls of its pores.

In Fig. 3 and Fig. 4, it is presented the angular dependences of the ellipsometric parameters $\cos\Delta$ and $\mathrm{tg}\Psi$ for the samples of PS with different degree P of porosity before and after surface treatment by isopropyl alcohol obtained near the principal angle of light incidence.

It is seen that as a result of an interaction of isopropyl alcohol with a sample surface and subsequent keeping of samples in air atmosphere the angular dependences of the ellipsometric parameters somehow change.

In particular, the maximal decrease of the principal angle of light incidence (about of 0.5-0.9°) for both samples of PS occurs after their keeping in air atmosphere during 2 months. It is probable that the observed changes in the behavior of the ellipsometric curves are due to changes in atomic and electronic structure and appropriate topological parameters of the subsurface layer of PS owing to the penetration of the liquid (alcohol) into this subsurface layer. In accordance with the relationship $n = \sin\varphi_p \mathrm{tg}\varphi_p \cos 2\Psi_p$ the refractive index of PS after such treatment should be diminished.

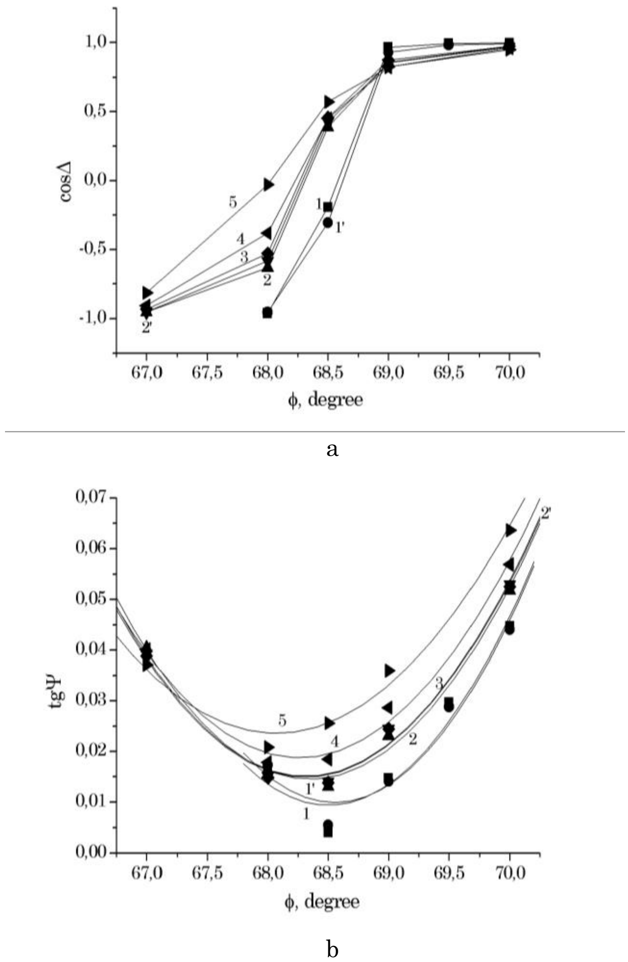

Fig. 3 – Dependences of cosΔ(φ) (a) and tgΨ(φ) (b) for PS sample with $P = 30$ % before surface treatment by isopropyl alcohol (date of measurements: 03.05.2019 – 1 ($\alpha = 0°$), 1′ ($\alpha = 90°$)) and after it (measurements dates: 15.05.2019 – 2 ($\alpha = 0°$), 2′ ($\alpha = 90°$); 22.05.2019 – 3 ($\alpha = 0°$); 07.06.2019 – 4 ($\alpha = 0°$); 02.07.2019 – 5 ($\alpha = 0°$))

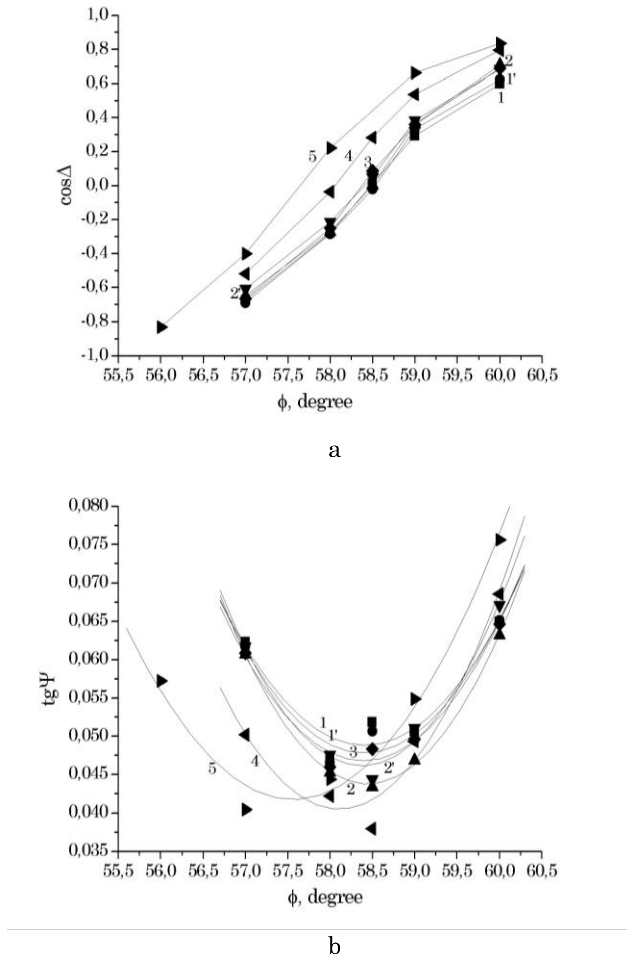

Fig. 4 – Dependences of cosΔ(φ) (a) and tgΨ(φ) (b) for PS sample with $P = 60$ % before surface treatment by isopropyl alcohol (date of measurements: 18.04.2019 – 1 ($\alpha = 0°$), 1′ ($\alpha = 90°$)) and after it (measurements dates: 10.05.2019 – 2 ($\alpha = 0°$), 2′ ($\alpha = 90°$); 22.05.2019 – 3 ($\alpha = 0°$); 07.06.2019 – 4 ($\alpha = 0°$); 02.07.2019 – 5 ($\alpha = 0°$))

Apparently after the alcohol penetration into the pores of PS samples some part of pores instead of air atmosphere is substituted by liquid (alcohol) with higher refractive index (of the order of 1.37) that should lead to an increase in the effective refractive index, and hence the principal angle of light incidence φ_p of the surface layer of the PS. At the same time, cause of the opposite behavior of the optical properties of PS after treatment by isopropyl alcohol is observed due to its further evaporation in air atmosphere and probable oxidation of silicon. The growth of some amount of silicon oxide, which possesses much smaller refractive index of 1.46 in comparison to that of silicon ($n = 3.88$), could cause the significant decrease of the principal angle of light incidence as well as the effective refractive index of the surface layers of PS after samples processing in isopropyl alcohol during one day and then at their further keeping in air atmosphere.

To a certain extent, our above-mentioned suggestion with respect to oxidation effect is confirmed by data published in work [3] where the PS surface was modified by another organic substance, namely aqueous solutions of nucleic acids. This similar effect due to the photoluminescence behavior as a result of such modification on the PS was studied and also explained by the oxidation process influence. The nucleic acid has stimulated some increase of photoluminescence intensity in the PS which was attributed to thinning of the silicon skeleton in consequence of silicon oxidation.

4. CONCLUSIONS

It was established for PS that a twofold difference in the degree of porosity leads to the significant difference in optical properties of the surface layer. The effective refractive indices n of the PS samples obtained in the model of a filmless semi-infinite reflective medium for the samples with $P = 30$ % and $P = 60$ % were equal to 2.40 and 1.40 respectively.

The treatment of the samples of PS in isopropyl alcohol during one day and ther further keeping in air atmosphere leads to some decrease of the principal angle of light incidence and the effective refractive index due to oxidation process within surface layer of PS.

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Кутова еліпсометрія поверхневих шарів поруватого кремнію

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Проведено еліпсометричну діагностику зразків поруватого кремнію з різним ступенем поруватості *P*. Зразки поруватого кремнію зі ступенем поруватості 30 % та 60 % було отримано на пластинах кремнію (100) з *p*-типом провідності, допованих бором високої концентрації, шляхом травлення у розчині HF та етанолу. Для характеризації оптичних властивостей зразків поруватого кремнію вимірювались кутові залежності таких еліпсометричних параметрів як Δ (cosΔ) та Ψ (tgΨ) в широкому інтервалі кутів падіння світла. З їх кутових залежностей визначались головний кут падіння світла φ_p та величина $\mathrm{tg}\Psi_{min}$ і її кутове положення. Також було досліджено оптичні властивості зразків поруватого кремнію з різним ступенем поруватості після їх витримування в ізопропіловому спирті протягом однієї доби. Морфологію поверхні зразків поруватого кремнію було досліджено методом атомно-силової мікроскопії. Знайдено, що еліпсометричні параметри для цих двох зразків поруватого кремнію з різним ступенем поруватості суттєво відрізняються, а саме відмінність у величинах головного кута падіння світла та кутового положення мінімуму tg*Ψ* складає порядку 10°. В рамках моделі ефективного середовища одержані результати пояснено наявністю у зразку поруватого кремнію з *P* = 60% великої кількості речовини з малим показником заломлення, а саме повітря та оксиду кремнія, що утворився на стінках пор. Встановлено, що обробка зразків поруватого кремнію ізопропіловим спиртом протягом однієї доби з подальшим витримуванням зразків у повітрі призводить до зменшення головного кута падіння світла та показника заломлення внаслідок окислення поруватого кремнію.

Ключові слова: Поруватий кремній, Оптичні властивості, Окислення, Плівка, Еліпсометрія.