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Studies of Porous Silicon Aging by Ellipsometry

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What problem was solved

The object of this study deals with the process of forming a thin film on a surface of the porous silicon (PS) sample formed by a long time of its staying in the air atmosphere.

What is installed

A film grows on the porous silicon surface as a result of exposure to air. The structure of the film can be represented as a set of two layers with different refractive indices and thickness (Fig. 1).

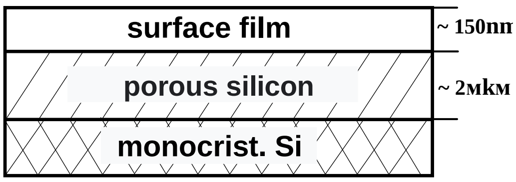

Рис. 1. The structure of the subsurface region PS

Experimental details

Porous silicon (PS) is obtained by electrochemical etching of single crystalline silicon in an electrolyte based 48%HF+ acetone (2:1, sample 1) or isopropyl alcohol (1:1, sample 2 and 3) when a low-density electric current 10 мA/см^2 is passed through it during 3 – 5 minutes . Specific technological parameters for obtaining samples are given in table 1.

Table 1.

Sample age, months	Sample number	Current density, mA/cm^2	Electrolyte composition	Formation time, min	Porosity
2,5	1	10	HF+acetone,2:1	3	67%
7	2	10	HF+isopr alk,1:1	5	?
7	3	10	HF+isopr alk,1:1	3	?

The sample after preparation and cleaning has been in the air atmosphere during more than one year and aging process has been reached. A bright interference pattern was observed on the surface of the samples, which is characteristic of films with variable thickness over their area.

How it was obtained

The study was performed using non-standard ellipsometer with the wavelengths of 405, 435 and 579 nm. The measured values are the ellipsometric parameters – the phase difference Δ between the p- and s- components of the reflected wave electric vector as well as the tgψ, ratio of the amplitude reflection coefficients in the p- and s-planes of the sample. The measurements were performed within a range of light incidence angles φ. The measurements began a few months after the samples production and were repeated periodically for several years.

Results

The obtained data due to aging process for PS sample are shown in figure 1 for samplei 1 in the form of the ellipsometric curve, namely angular dependences of the ellipsometric parameter tgψ. It is seen that the angular functions of the ellipsometric parameter tgψ undergo considerable changes due to result of the film aging. In particular, the maximum of the tgψ function 579 nm decreases in amplitude and becomes the minimum. A similar aging result was obtained for sample 2 and 3.

The curve cosΔ(φ) varies little, so they are not listed here.

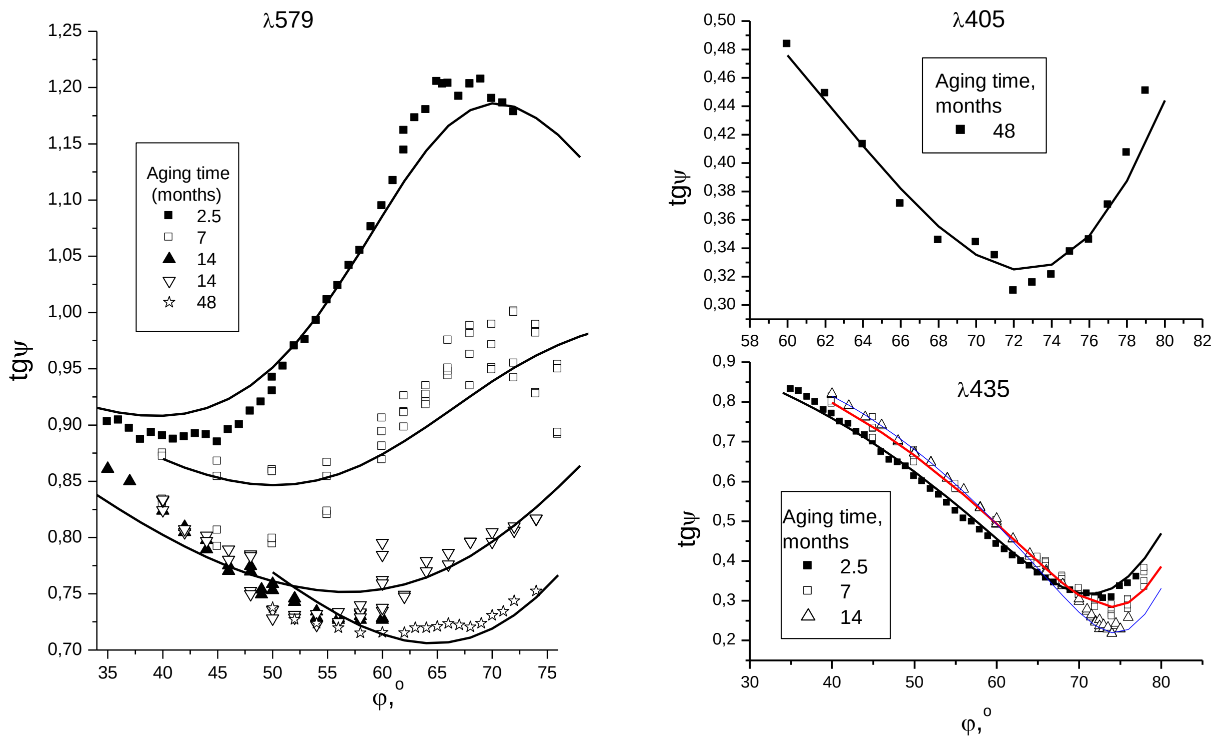

Fig 1. Dependence of the ellipsometric parameter tgψ (symbols) on the angle of incidence φ for sample 1, measured at different points in time at three wavelengths 579, 435 and 405 nm in comparison with theoretical calculations (solid curves)

This ellipsometric curves transformation (effect of aging) may be caused by change of surface layer parameters during the interaction of the electrochemical reactions products with the basic material, the atmospheric air (oxygen, water vapor) and atmospheric air with substrate (silicon).

The films parameters finding

Single- and two-layer reflective system models were used to adequately explain the obtained data.

It was found in a single-layer model that both the thickness and the refractive index obtained from measurements at different angles of light incidence depend on such angle monotonically. Therefore in such case the single-layer model describes the real structure of the investigated PS sample only approximately.

Finding of the films parameters on the two-layer model were based on a gradient method of the minimum finding for the function namely determined by the variation of the measured values due to measurement error (so-called functional)

$$\Phi = \frac{1}{2N}\sum_{i=1}^{N}\left\{(tg\psi_{iE} - tg\psi_{iT})^2 + (\cos\Delta_{iE} - \cos\Delta_{iT})^2\right\} \quad (1),$$

where N is the number of measurements (in this case the set of the angles of light incidence) and the indices E and T are referred to the experimental and theoretical values of appropriate ellipsometric parameters respectively.

Several possible solutions appear in the process of automated data processing. We provide data for system parameters (table. 2) that correspond to the minimum of the residual function (1).

Табл. 2. Refractive indices n_1, n_2 and thickness d_1, d_2 outer and inner layers, minimum value of the factorial F0 and gradient G in the minimum of factorial

Aging time (months)	Outer layer		Inner layer		F0	G (grad)
	n_1	d_1, nm	n_2	d_2,nm		
Sample №1						
2.5 λ579	1.071	171.9	1.923	67.1	0.0013	0.0017
2.5 λ435	1.120	103.5	3.00	45.3	0.000230	0.0000022
7 λ579	1.113	86.3	1.792	59.5	0.0056	0.000227
7 λ435	1.2635	66.7	2.1657	88.8	0.000166	0.000123
14 λ579	1.1207	133.1	2.2443	50.5	0.000145	0.001112
14 λ435	1.2038	82.6	2.1014	87.3	0.000389	0.000008
47 λ579	1.0860	100.0	1.8040	50.8	0.000088	0.000030
48 λ579	1.0967	106.5	1.9135	49.4	0.000331	0.000002
48 λ405	1.0845	112.9	3.436	30.0	0.000241	0.000021

Factorial F0 characterizes the minimum achieved data scattering relative to the found theoretical curve. The nearness of the gradient F0 to zero indicates the achievement of a minimum. Figure 1 shows a comparison of experimental data with theoretical curves calculated from the found parameters of the layers.

Discussion and conclusions

It is seen from the data presented in table. 2, that in all cases sufficiently small values of the functional and its gradient are achieved.

The large scattering of the obtained the film parameters values may indicate its inhomogeneity in thickness, as well as the sensitivity of the film to atmospheric conditions during measurement. It can be argued that the refractive index of the upper the film layers are significantly less than the refractive index of the lower ones.

In particular, the value of the refractive index of the upper layer, close to 1.1, is explained by the presence of air in the film thickness. If we assume that the film contains only oxides of silicon (refractive index close to 1.4) and air, the value of the refractive index of the upper layer of the film 1.11 corresponds to a porosity of 70%.

The results obtained may be relevant for the creation of sensors that respond to the state of the atmosphere and other liquid or gaseous compounds.