

Effect of the Porous Silicon Layer Structure on Gas Adsorption

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The paper deals with the study of the effect of the morphology and structure of crystallites of *p*-Si layer on the adsorption of gas sensors. The porous layer was obtained by electrochemical anodization at anodizing current from 10 to 60 mA and anodizing time from 5 to 30 min. The sensors were created as *p*-Si structures: PdAu-Si:GeAuNiAu by electron-beam evaporation. The porous layer surface was studied with optical microscopy, and the crystallite structure was examined with FTIR technique. It has been discovered that the anodization modes have a direct effect on the deformation vibrations of the SiH_x group in wavenumbers from 700 to 950 cm⁻¹. At the boundaries of the crystallites, compressing stresses arise causing a decrease in Si–O–Si bond in wavenumbers from 1060 to 1160 cm⁻¹. It has been demonstrated the increasing effect of SiH_n stretching bonds and SiO_xH_y complexes (absorption peaks at 2116 cm⁻¹ and 2340 cm⁻¹ respectively). The variation of anodizing time has a stronger effect on the structure of the porous layer than the variation of anodizing current. The adsorption sensitivity of the porous layer has been determined by the relative change in conductivity. The data obtained make it possible to conclude that the anodization mode affects the adsorption of gas sensors. This conclusion correlates with the data obtained with FTIR method in crystallites structure.

Keywords: Porous layer, Sensor, Silicon, FTIR spectroscopy.

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1. INTRODUCTION

Porous silicon (*p*-Si) is a silicon substrate with a layer created on it by various methods. This layer is a Si-based adsorbent with optimal electrical and optical properties, it has a high surface-to-volume ratio, which allows its properties to be used for manufacturing adsorption-based devices, in particular gas sensors [1, 2], humidity sensors [3], organic liquid sensors [4], sensors for non-invasive diagnostics in medicine [5, 6].

Porous silicon layers are typically obtained by electrochemical anodization in acid like HF. Anodization is performed in an electrochemical cell during a certain time under direct or pulsed current of required density [7]. It results in the formation of layer morphology, which defines the structure of the layer surface and internal geometry. In the paper [8], the influence of the porous layer morphology on the properties of the Schottky contact has been investigated with photoluminescence, electron and optical microscopy.

The parameters of gas sensors, such as adsorption, sensitivity, selectivity, and sampling time are attributed to the layer morphology and crystallites structure. The size and structure of crystallites specify the electrical and optical properties of the sensors. To study the crystallites structure, it is convenient to use Fourier transform infrared (FTIR) spectroscopy [9]. This method is useful due to silicon transparency for IR light. The method allows getting information on chemical bonds of crystallites with hydrogen and oxygen, which are formed during anodization and drying.

The paper presents the measurement procedure and IR spectra of absorption bands for various electrochemical anodization modes, as well as the dependence of conductivity on an anodization mode, gas composition, and pressure. Also, the dependence of gas sensor adsorption on porous layer properties is analyzed.

2. DESCRIPTION OF EXPERIMENTAL SAMPLES MANUFACTURING

N-type silicon substrates of SEP-10 (111) grade were used as samples. The diameter and thickness of the substrate were respectively 76 mm and 420 μm. In total, 5 samples were manufactured.

All samples were treated with electrochemical anodization to obtain a porous layer during one day. Before the formation of the porous layer, the samples were degreased by sequential immersion in organic solvents of trichloroethylene, acetone, and methanol. Then they were washed with deionized water and dried with dry nitrogen for 10 min.

A porous layer with an area of 6.28 cm² was created in a vertical-type electrochemical cell. Anodization was controlled with a fuzzy control system [10]. The etching area was illuminated with a 100 W halogen lamp. The modes of samples anodization are given in Table 1.

After anodization, the *p*-Si samples were cleaned with ethanol and dried in air. The anodization parameters were not specific, but, in our opinion, they allowed us to obtain some information on changes in porous layer properties with a variation of the anodizing parameters.

Table 1 – Modes of samples anodization

Sample No	Grade	Etchant composition	Etching mode current (mA)/time (min)
1	SEP-10 (111)	HF:C ₂ H ₅ OH (1:1)	10/5
2	SEP-10 (111)	HF: C ₂ H ₅ OH (1:1)	30/5
3	SEP-10 (111)	HF: C ₂ H ₅ OH (1:1)	60/5
4	SEP-10 (111)	HF: C ₂ H ₅ OH (1:1)	30/20
5	SEP-10 (111)	HF: C ₂ H ₅ OH (1:1)	30/30

The surface of the porous layer was studied with SZM 745 binocular stereo microscope, the depth of the porous layer was measured with MII-4 microinterferometer with an optical magnification 500 \times , equipped with DLT-Cam digital microscope camera and DLTCamViewer software using an OM-O object micrometer for software calibration. Photoluminescence spectra were measured at ambient temperature with MDR-24 spectrophotometer. The porosity of the layer was determined by the gravimetric method on AXIS ANG200C scales. Infrared spectra were obtained at ambient temperature with FSM 1201 IR Fourier spectrometer in the spectral range 400-7800 cm^{-1} with a resolution of 1 cm^{-1} .

The electron-beam evaporation was used to create AuNiAuGe ohmic contact to a silicon wafer with layers thickness of 100/20/80/20 nm respectively, followed by annealing in a nitrogen atmosphere at a temperature of 400 $^{\circ}\text{C}$. Contacts to the porous layer were also created by AuPd electron-beam evaporation with layers thickness of 50/20 nm. The structure of the samples is shown in Fig. 1.

The conductivity of the samples was measured with a P4833 universal measuring device in the resistance box mode.

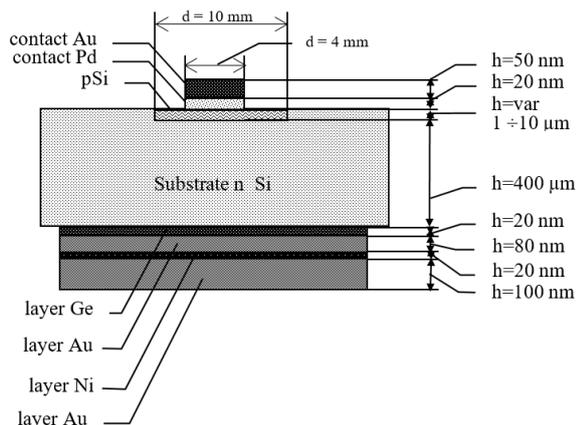


Fig. 1 – Schematic presentation of the sample: d – diameter of the porous layer and diameter of the contact; h – the height of metal contacts evaporation; l – the height of the porous layer

3. RESULTS AND DISCUSSION

Gas concentration increase at the interface between the gas phase boundary and the surface of the porous silicon film during adsorption leads to a change in the electrophysical properties of the crystallites making up the porous film. This process results in the redistribution of electron and hole concentration, which in turn leads to a change in conductivity.

The properties of a porous silicon film are affected by many factors, such as etching parameters, crystal orientation, dopant type, current density, etching solution, and time. The authors began to study the effect of the porous layer structure on gas adsorption with exploring the influence of the anodization modes on the layer porosity. The anodization modes of the samples are given in Table 1.

An analysis of the results obtained with an optical microscope has shown that an increase in the anodizing current density at the fixed time leads to an increase in the uniformity of the porous layer (Fig. 2a, b), but then some violations of the layer uniformity appear (Fig. 2c). An increase in the anodizing time at fixed current density leads to two different regions on the layer: black and white. The morphology of these regions is different like in Fig. 2d, e. The black region represents islands with uniform morphology and occupies most of the surface of the porous layer. The white region contains a random set of crystallites. In our opinion, the reason for this region is an uneven distribution of the dopant while a semiconductor ingot was growing. Anodizing time rising to 20 min at the current density of 30 mA/cm^2 leads to increasing the time of acid-silicon surface interaction, and as a result, changing the etching rate of various regions of the layer.

The porosity of the obtained porous layers was determined by the gravimetric method, based on the technique proposed in [11]. We have slightly changed it to exclude porous layer etching under the following equation:

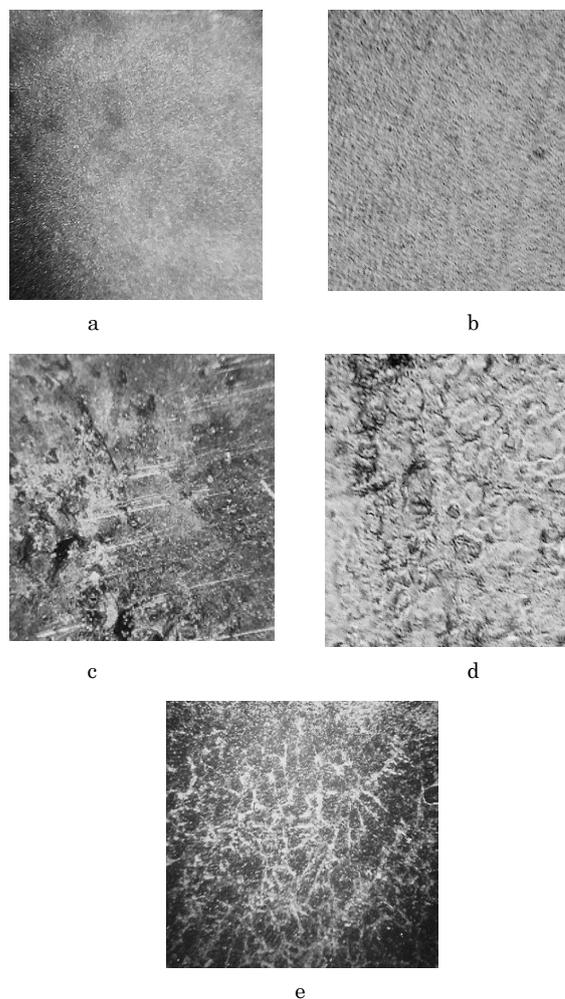


Fig. 2 – Optical image of p -Si layer with a magnification 47 \times at various anodizing current density and anodizing time: the sample No 1 (a); the sample No 2 (b); the sample No 3 (c); the sample No 4 (d); the sample No 5 (e)

$$P(\%) = \frac{(m_1 - m_2)}{\rho Sh} \times 100\%, \quad (1)$$

where ρ is the density of Si ($\rho = 2.33 \text{ g/cm}^3$), S is the area of p -Si layer (0.78 cm^2), h is the height of the porous layer. The height of the porous layer was measured on the fracture of satellite structures on which the porous layer was created under identical anodizing conditions. The measurements were carried out with DLTCamViewer software by counting the pixels in the fracture image obtained with MII-4 microscope with DLT-Cam digital camera. The measurement results are presented in Table 2.

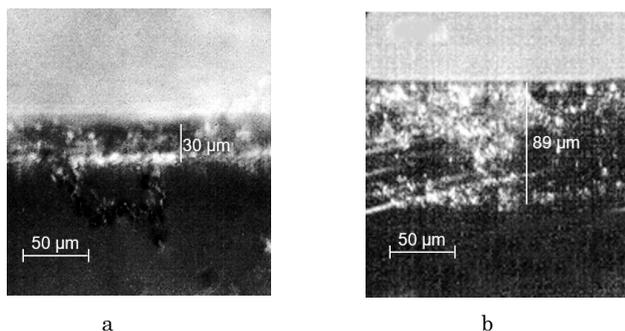


Fig. 3 – Optical image of the p -Si layer with a magnification $500\times$ at different anodizing current density and anodizing time: the sample No 1 (a); the sample No 5 (b)

Table 2 – Results of structures porosity calculation

No	Sample mass before anodizing m_1 , g	Sample mass after anodizing m_2 , g	Porous layer height, $\text{cm} \times 10^{-4}$	Porosity, %
1	1.1223	1.1187	30	65
2	0.8897	0.8822	46	68
3	1.1680	1.1601	59	73
4	1.0630	1.0529	71	78
5	1.1394	1.1254	89	86

In order to obtain data on chemical bonds in the porous layer and their possible deformations, we used IR spectroscopy. The studies were carried out with FTIR, which is better than IR dispersion in sensitivity, sampling time and resolution (Fig. 3).

In all samples, in the range $580\text{-}1200 \text{ cm}^{-1}$, six absorption bands are visible: two bands with clear peaks at 605 cm^{-1} and 1110 cm^{-1} ; two unclear bands in the range $700\text{-}950 \text{ cm}^{-1}$ with peaks at 708 cm^{-1} and 910 cm^{-1} ; and two bands in the range $2100\text{-}2400 \text{ cm}^{-1}$ with peaks at 2116 cm^{-1} and 2340 cm^{-1} .

The absorption peaks of the first band are attributed to carbon bonds which are formed during ingots growing with a graphite heater. The configuration of carbon bonds in silicon is characterized by Td symmetry. In the IR spectrum, one antisymmetric valence vibration is active, whose frequency is 605 cm^{-1} . Since carbon in silicon is electrically neutral, the absorption peaks do not vary in all samples practically, this testifies to unchangeable behavior of carbon bonds under various anodizing time.

Two absorption bands in the wavenumber range $700\text{-}950 \text{ cm}^{-1}$ have peaks at 708 cm^{-1} and 910 cm^{-1}

caused by SiH groups. The absorption of the first peak is caused by deformation vibrations of the SiH_x group [12], and of the second is due to SiH_2 scissors bending. It can be seen that a rise in anodizing current makes SiH group more influential. This effect can be explained by SiH_x complexes formation in crystallites due to HF treatment during anodization. This is also proved by the absorption range [13] $2400\text{-}2500 \text{ cm}^{-1}$, in which peaks are caused by SiH_n stretching bonds $n = 1.2.3$ (absorption peak 2116 cm^{-1}) and SiO_xH_y complexes (absorption peak 2340 cm^{-1}). At the same time, there are no such bonds in the sample, which was not anodized. Therefore, they appear during anodization, and they are increasing with higher etching current.

The broad absorption peak at 1110 cm^{-1} is attributed to the presence of oxygen in silicon, which, like carbon, gets into the ingot during growing by the Czochralski method. The behavior of oxygen bonds is different from the behavior of carbon bonds. But carbon bonds are not practically changeable during anodization, whereas the oxygen bonds peaks are increasing with higher etching current. Taking into account that during anodization oxygen does not get into crystallites from the solution, the effect of peak rising can be explained by the following reasons. Firstly, there is an effect of “post-oxidation”, which becomes apparent in porous layer oxidation during drying in air. Since the volume of the porous layer increases with higher etching current (see Table 2), the layer area subjected to oxidation increases accordingly. Secondly, compressing stresses arise at the crystallite edges during anodization, which causes a decrease in the middle angle of Si–O–Si tetrahedral bond [14]. The compression of oxygen structures is not associated with a change in SiO bond.

An increase in the anodizing time at a constant current indicates that the main dependencies are not changeable. The effect of hydrogen and oxygen bonds is increasing. Anodizing time increase to 30 min leads to absorption band widening in the region of low wavenumbers in the range $590\text{-}690 \text{ cm}^{-1}$. This demonstrates an increase in the effect of deformation vibrations of SiH_x groups with different local environments, as well as pendular oscillations and wagging vibrations of SiH_2 group.

The influence of deformation vibrations of SiH_x group and SiH_2 scissors bending with peaks at 708 cm^{-1} and 910 cm^{-1} is especially strong. This effect is caused by a longer HF treatment in the anodization process. The effect of SiOSi complexes in the wavenumbers range $1060\text{-}1160 \text{ cm}^{-1}$ is intensified similarly. It is caused by an increased impact of the “post-oxidation” effect and stronger compressing stresses. The influence of SiH_n stretching bonds and SiO_xH_y complexes (absorption peaks at 2116 cm^{-1} and 2340 cm^{-1} , respectively) also increases significantly.

Thus, we can conclude that anodizing time variation has a greater effect on the structure of the porous layer than anodizing current variation. Oxidation of crystallites leads to compressive stresses, which are increasing with longer etching time.

Adsorption in a porous silicon layer occurs whenever gas affects the pores of the layer. Under certain conditions, there is a noticeable increase in the concentration of a particular component in crystallites edges, and

the overall effect depends on the morphology of the porous layer. A change in gas pressure around the sensor or gas concentration leads to a change in the concentration of free charge localized at the levels created in the forbidden zone by the adsorbed particles, and the electrical properties of p -Si/ c -Si structure.

Porous silicon has a large surface area, and a large surface area provides very high sensitivity of adsorbed molecules on the surface. To determine the porous layer adsorption sensitivity to pressure variations, gas concentration or porous layer morphology, the ratio for relative change in conductivity is used

$$\gamma_G = \frac{1}{G_H} \frac{\Delta G}{\Delta p}, \quad (2)$$

where G_H is the electrical conductivity at the initial pressure or gas concentration; $\Delta G = G_H - G_i$, G_i is the conductivity at the measurement point; Δp is the variation of the partial pressure of the controlled gases.

Experimental studies of the effect of the porous layer morphology on adsorption have been carried out with a gas station according to the following scheme (Fig. 4).

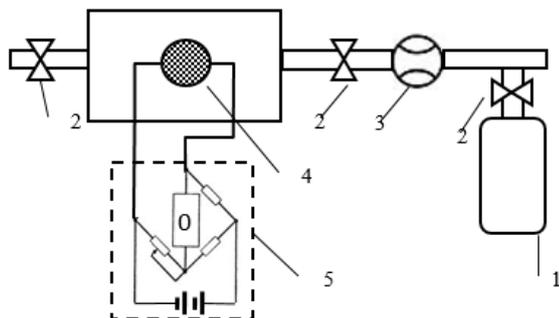


Fig. 4 – Installation for gas adsorption study: 1 – a cylinder with a test gas mixture; 2 – cranes; 3 – a gas pressure gage; 4 – a p -Si sensor; 5 – a P4833 resistance box

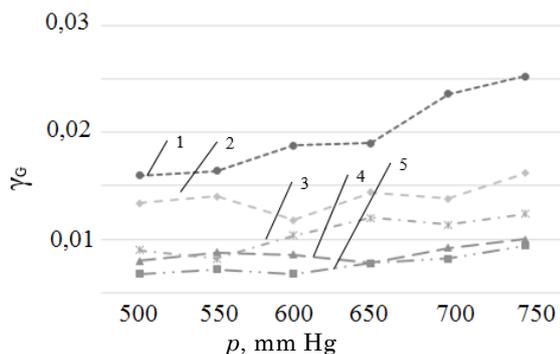


Fig. 5 – The hydrogen effect on the relative change in p -Si conductivity: 1 – the sample No 1; 2 – the sample No 2; 3 – the sample No 3; 4 – the sample No 4; 5 – the sample No 5

To study the adsorption of the porous layer of the samples, test gas mixtures of methane (CH_4) and hydrogen (H_2) have been used. The measurements have been carried out at a partial gas pressure in the range 500-750 mm Hg with increments of 50 mm Hg. Conductivity has been measured with P4833 resistance box

which has a measurement error of $\pm 0.1\%$ in the required resistance range, then the relative change in conductivity was measured by equation (1). The results obtained for hydrogen and methane are shown in Fig. 5 and Fig. 6, respectively.

The analysis of the data received shows that in all samples the conductivity increases with higher porosity. The porous layer is becoming deeper with increasing anodizing current and time. Moreover, as in the case of the analysis of IR spectra, an increase in the anodizing time leads to a more evident effect.

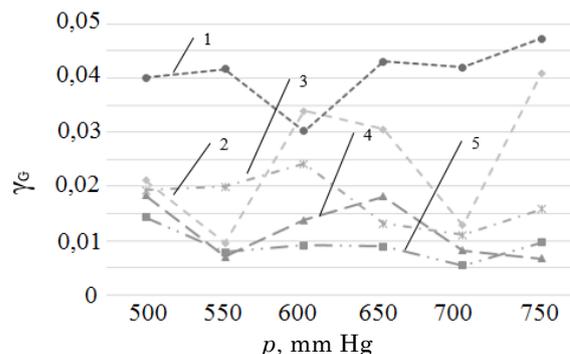


Fig. 6 – The hydrogen effect on the relative change in p -Si conductivity: 1 – the sample No 1; 2 – the sample No 2; 3 – the sample No 3; 4 – the sample No 4; 5 – the sample No 5

As it has been shown above, the longer the anodizing time, the more influential SiO_x complexes become. When crystallites are oxidized, Si-OH groups are formed on its surface, and SiO_x groups – in the surface interface layer. These hydroxyl groups make hydrogen adsorption better. It can be assumed that the effect of hydrogen bonds in the wavenumber range $2100\text{-}2400\text{ cm}^{-1}$ also contributes to adsorption enhancement.

4. CONCLUSIONS

The paper discusses the effect of p -Si morphology on the adsorption of a porous layer. The study has been carried out on five samples of p -Si structures: PdAu-Si: GeAuNiAu whose porous layers were manufactured under various anodizing current and time. The IR spectroscopy helped to find out that the anodizing time has a more evident influence of hydrogen and oxygen complexes than the anodizing current. Oxygen bonds arising during oxidation of crystallites after anodization lead to the formation of hydroxyl groups, which contributes to adsorption enhancement.

A correlation has been established between the sensors conductivity and the anodization modes, and the composition of the gas acting on the sensor. This makes possible to use the sensor's conductivity to measure the concentration of pure gases and gas mixtures. By varying the anodization modes, it is possible to change the parameters of p -Si gas sensors.

The studies have revealed the possibility of manufacturing p -Si-based gas sensors for industrial and environmental applications, as well as for invasive disease diagnostic systems in medicine.

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Вплив структури поруватого шару кремнію на адсорбцію газів

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Досліджувався вплив морфології і структури кристалітів пористого шару p -Si на адсорбцію сенсорів газу. Поруватий шар отримували електрохімічним анодуванням при варіації струму анодування в діапазоні 10-60 мА і часу анодування в діапазоні 5-30 хв. Сенсори створювалися як структури p -Si: PdAu-Si:GeAuNiAu методом електронно-променевого напilenня. Методом оптичної мікроскопії досліджувалась поверхня поруватого шару і методом FTIR досліджено структуру кристалітів. Установлено, що режими анодування безпосередньо впливають на деформаційні коливання групи SiH_x в діапазоні хвильових чисел 700-950 см⁻¹. На межах кристалітів виникають стискаючі напруги, які викликають зменшення зв'язку Si-O-Si в діапазоні хвильових чисел 1060-1160 см⁻¹. Показаний ефект зростання впливу розтягувальних зв'язків SiH_n і комплексів SiO_xH_y (піки поглинання 2116 см⁻¹ і 2340 см⁻¹ відповідно). Варіація часу анодування надає більш сильний вплив на структуру поруватого шару, ніж варіація струму анодування. Визначення адсорбційної чутливості поруватого шару проводилося по значенню відносної зміни провідності. Отримані дані дозволяють зробити висновок про вплив режиму анодування на адсорбцію газових сенсорів, які корелюються з даними, отриманими методом FTIR, для структури кристалітів.

Ключові слова: Поруватий шар, Сенсор, Кремній, Інфрачервона Фур'є спектроскопія.