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# Investigation of the physical properties of nanoscale porous silicon films

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The structure and physical properties of porous silicon obtained by electrochemical etching of monocrystalline silicon with n-type conductivity in a mixture of hydrofluoric acid and ethyl alcohol were investigated. Experimental layers were formed by varying the etching parameters. Samples were studied using the methods of atomic force microscopy (AFM),scanning electron microscopy (SEM), Raman spectroscopy (RS) and photoluminescence spectrometry (PL). It was found that the PL intensity increased with increasing etching time.It was demonstrated that by varying of technological parameters and conditions of the etching process we can control the size of nanocrystals and manufacture nanostructuresof porous silicon film with improved properties.

Key words: porous silicon, electrochemical etching, photoluminescence, nanocrystals.
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## 1 Introduction

Porous silicon (PS) attracted the attention of researchers for the most part due to its luminescent properties [1]. In addition, the extensive study of various properties of the PS has opened prospects for its numerous alternative applications in areas such as solar cells, biotechnology, sensors [2,3]. Well-developed method of electrochemical etching of silicon allows controllable vary parameters of porous layer in order to optimize its physical properties. The surface morphology of the PS film and its structural and optical properties depend on the such parameters like the concentration and type of impurity in the initial silicon substrate, the magnitude of the anodizing current and the duration of etching, the composition and temperature of the electrolyte, and other factors [4].

Using of Raman spectroscopy allows us to estimate the characteristic dimensions in PS nanocrystals and their dependence on technological regimes for producing PS with different properties. More information about the morphology of the surface of semiconductor films can be obtained using the method of atomic force microscopy [5,6].

This paper presents the results of studies of the structure, morphology and photoluminescence properties of porous silicon films grown on n-type crystalline Si substrates for different values of the duration and magnitude of the anodizing current.

## 2 Experimental Details

N-type silicon wafers with a phosphorus concentration $10^{18}$ $cm^{-3}$ and the crystallographic orientation (100) were used for manufacturing PS. Before anodization a silicon wafers were placed to trichloroethylene for degreasing, were rinsed in deionized water, then after treatment in a solution of $H_2SO_4$: $H_2O_2$ (4: 1) at temperature $90^0$C for 10 minutes silicon wafers were etched in a mixture of HF and $H_2O$ (1: 50) for 10 seconds and thoroughly washed in deionized water. Etching occurred in the electrolyte containing hydrofluoric acid and ethyl alcohol in a ratio of 1: 1.5.

To determine the differences in the structure and properties of PS three groups of samples were prepared at different anodizing current densities and with different anodization time: 1 – J = 1 mA/$cm^2$, t = 20 min; 2 – J = 15 mA/$cm^2$, t = 2 min and 3 – J = 25 mA/$cm^2$, t = 1 min. The power supply voltage for all groups of samples remained unchanged at 10 V. These modes provide approximately the same ~1 micron thickness of PS. Measurements of the structure and properties of the PS samples were performed after 10 days storage in the air.

## 3 Results and discussion

The morphology of the films was studied using atomic force microscope NT-MDT NtegraTherma.

The study of PS surface morphology using the method of AFM has revealed its dependence on etching modes. Figure 1 shows the 3D image (1a, 2a, 3a) and the 2D image (1c, 2c, 3c) surface of PS films grown under the above conditions. Profile section along the center line shown in Fig. 1b, 2b, 3b for the three groups of samples.

Figure 1 shows that the prolonged etching under low current density of 1 mA/cm$^2$ (Fig. 1b) results in developed surface having a smaller size of structural heterogeneities than typical structures with less etching time, but with large current densities of 15 mA/cm$^2$ and 25 mA/cm$^2$ (Fig. 2b and 3b, respectively).

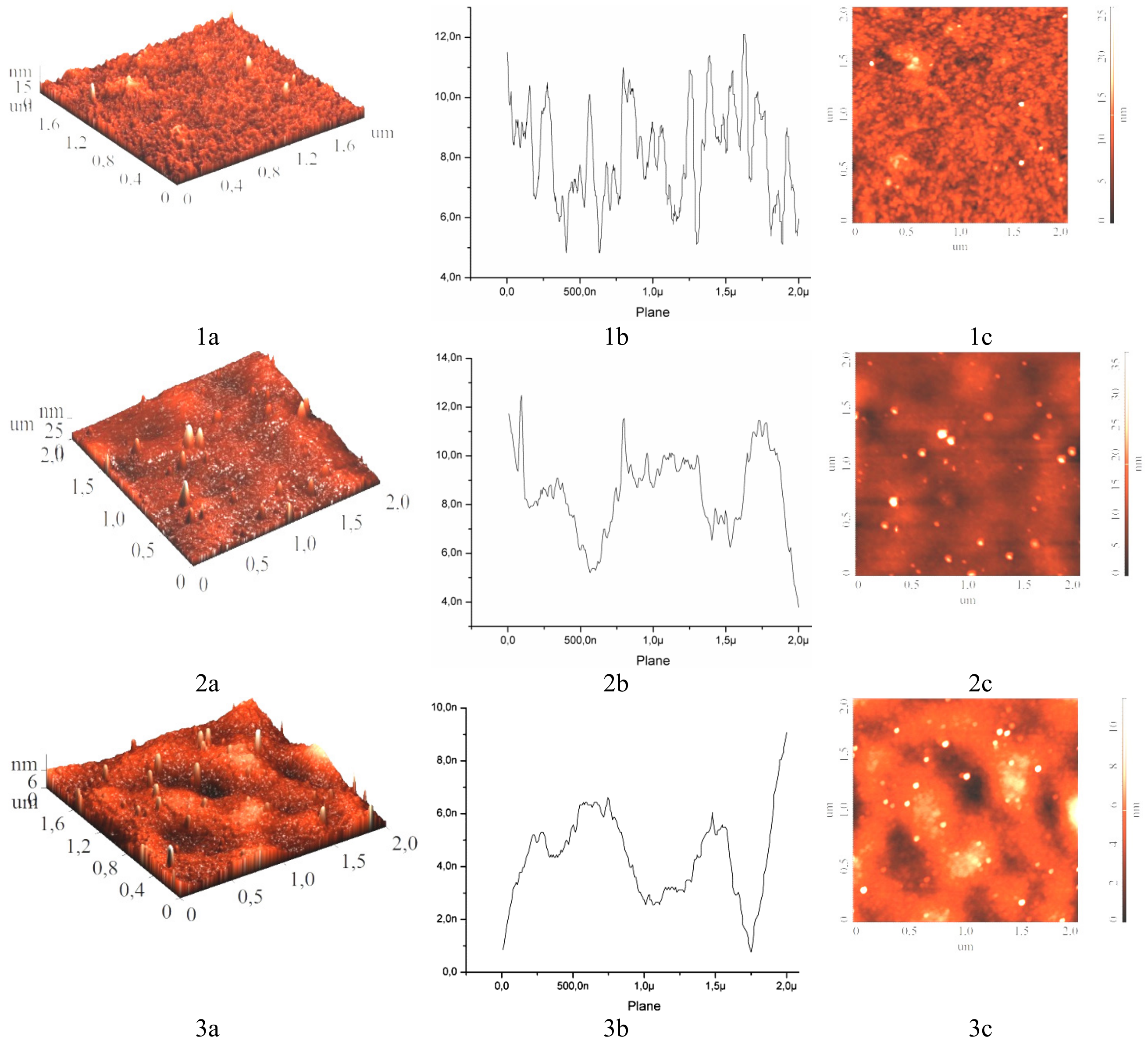


Figure 1 – AFM image of PS samples grown under different conditions for the three groups of samples:
1 – J = 1 mA/cm$^2$, t = 20 min.;
2 – J = 15 mA/cm$^2$, t = 2 min.;
3 – J = 25 mA/cm$^2$, t = 1 min.

For the mathematical characterization of the surface roughness we used the root-mean-square roughness $S_q$, defined as:

$$S_q = \sqrt{\frac{\sum_{i=1}^{N}\left(H_i - \hat{H}\right)^2}{N}}, \quad (1)$$

where $N$ is the number of measured points, $\hat{H}$ is the average height (zero level), $(H_i - \hat{H})$ is the relative height *of i* point.

The measurement results showed that the mean square roughness $S_q$for the sample groups 1,2 and 3 were 2.96 nm, 1.85 nm, and 1.63 nm, respectively.

Using image processing module of AFM height distribution functions for the investigated films were calculated for surface area of 2x2 μm$^2$ (Fig. 2).

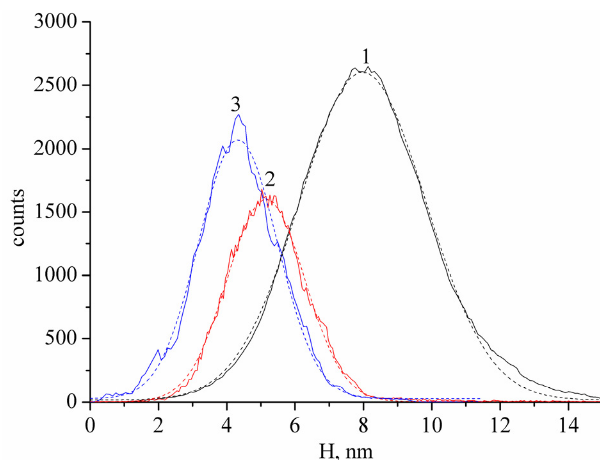


Figure 2 – Height distribution function of PS films for samples 1, 2, 3. Dashed lines are results of approximation with Gaussian functions

The distribution function for PS layers is well approximated by a Gaussian function centered at $H_1$ = 8.4 nm, $H_2$=4.8 nm, $H_3$ = 4.2 nm for samples 1, 2, 3, respectively. For sample 3 with the shortest etching time characteristic size of heterogeneity was minimal.

AFM images of the PS surface demonstrated that with increasing current density film surface becomes more smooth as compared with the PS produced at a current J = 1 mA/cm$^2$. Similarly to [7] the calibration experiments of porosity determination showed that when current density increases from J = 1 mA/cm$^2$ to J = 25 mA/cm$^2$porosity decreases from 50% to 30%, and typical dimensions are reduced from 8.4 nm to 4.2 nm.

Using an electron microscope FEI Quanta 200 FEG SEM-images of PS surface and cross-sectional samples were obtained. Figure 3 shows a cross-sectional view (a) and the surface of a PS (b), grown at a low current density. As seen in Fig. 3 the PS layers have sponge-like structure. The surface concentration of pores is uniform, and the sizes of pores were ranging from 7 nm to 9 nm. Samples obtained at high current densities characterized by a lower concentration of pores on the surface.

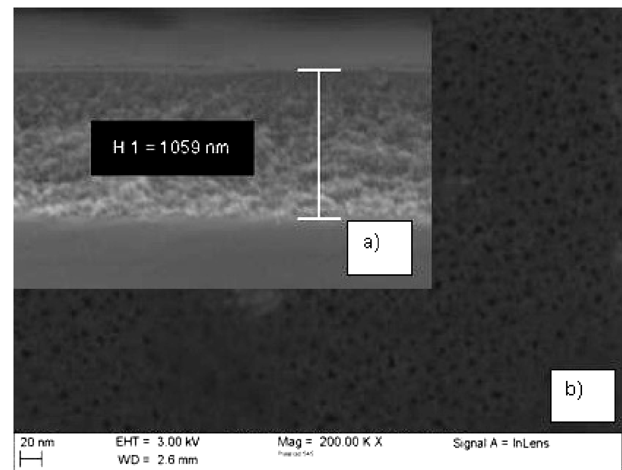


Figure 3 – SEM-images of cleaved facet (a) and surface (b) of PS sample grown at J = 1 mA/cm$^2$ for 20 min

Photoluminescence (PL) in PS is the evidence of PS band gap broadening due to the presence of nanoscale silicon clusters formed near the walls of the pores. Photoluminescence spectra were measured at room temperature using a spectrometer NT-MDT Ntegra Spectra, the incident laser power was about 25 mW at a wavelength of 477 nm. The diameter of the laser spot on the sample was about 2 microns.

Figure 4 shows the PL spectra for the three types of PS layers. For all samples, the shape of the PL spectrum is close to a Gaussian curve, maxima of the curves are in the range 650-680 nm, which corresponds to photon energy of 1.82 – 1.91 eV.

These peaks correspond to radiation in the red region of the spectrum and are explained on the basis of quantum confinement model [8].

The PL intensity of the peaks correlated with the duration of the etching, the maximum intensity was observed in the samples of group 1, which can be explained more porous, more advanced surface morphology and an increase in the concentration of nanocrystals.

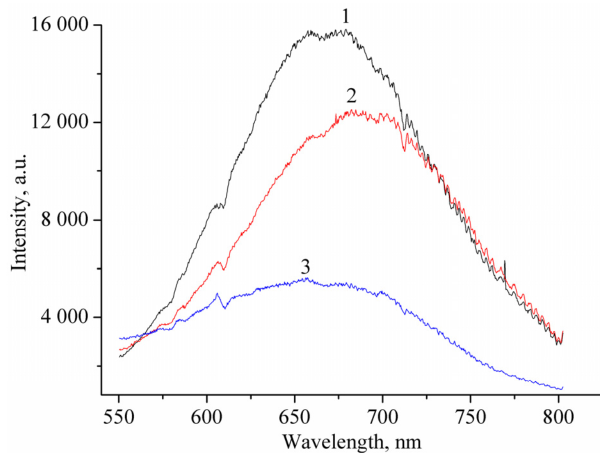


Figure 4 – Photoluminescence spectra of thePor-Si samples grown at different conditions:
1 – J = 1 mA/cm$^2$, t = 20 min.;
2 – J = 15 mA/cm$^2$, t = 2 min.;
3 – J = 25 mA/cm$^2$, t = 1 min

Reflectance spectra for all three groups of samples were recorded on a spectrophotometer Shimadzu UV-3600 and are presented in Figure 5.

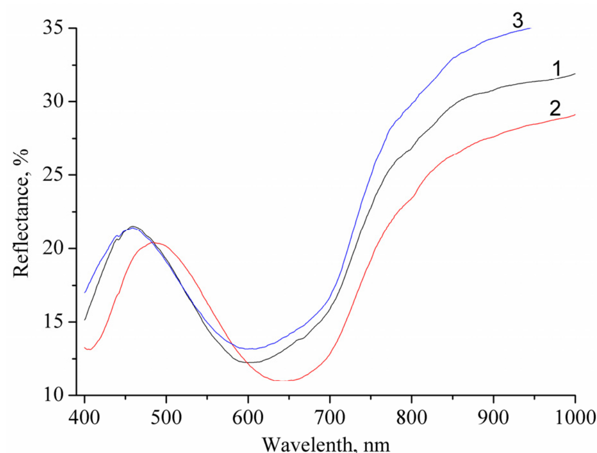


Figure 5 – Wavelength dependence of reflectance ofPS samples grown at different conditions:
1 – J = 1 mA/cm$^2$, t = 20 min .;
2 – J = 15 mA/cm$^2$, t = 2 min .;
3 – J = 25 mA/cm$^2$, t = 1 min

Position of the interference maxima and minima are in good agreement for all samples, indicating that their thicknesses are equal.

The Raman spectra of PS films is a good diagnostic tool for the study of structural phases and allows to evaluate the characteristic dimensions of the nanocrystals. The Raman peak from pure single-crystalline silicon was at 520 cm-1, and its shape was nearly Lorentz an. This peak is associated with longitudinal optical (LO) modes [7]. For porous silicon, the broadening and downshift of Raman peak towards lower energy are connected with the presence of nanoscale features of the crystalline structures. The Raman scattering experiments are performed in the range of 400-600 cm$^{-1}$ at room temperature using the spectrometer NT-MDT Ntegra Spectra and are shown in Figure 6. The peak at 514-518 cm$^{-1}$ (instead of 520 cm$^{-1}$) appears after etching the monocrystalline silicon and connected with nanoporous structure. Region 465-485 cm$^{-1}$ is associated with the transverse optical (TO)modes in the amorphous silicon [9].

For all samples of the PSshift in the position of the peaks in the Raman spectra to lower energy was observed. The greatest shift to 514 cm$^{-1}$ was observed for the PS layers with etching time of 20 minutes, for the samples with etching time of 1-2 minutes the peak shifts to 518 cm$^{-1}$.

Information on the average size of nanocrystallites in the PS can be obtained from the Cardona equation [10]

$$d = 2\pi \sqrt{\frac{B}{\Delta \omega}} \text{ (nm)}, \qquad (2)$$

where B = 2.24 cm$^{-1}$ for silicon, $\Delta\omega$ – the peak shift of Raman scattering in the PS relative to the peak of crystalline silicon. In accordance with (2) the PS crystallite sizes of the samples decreased from 6.6 nm to 3.8 nm with increasing etching duration of from 1 minute to 20 minutes.

Figure 6 shows that a decrease in the size of nanocrystals is accompanied with crystal imperfection, an expansion of the spectral line, which becomes more asymmetric and its maximum shifts to the lower energy. The broadening of the Raman spectra with increasing etching time indicates the violation of the crystal structure of silicon source, the appearance of the amorphous phase and nanocrystalline clusters on the surface of the pores.

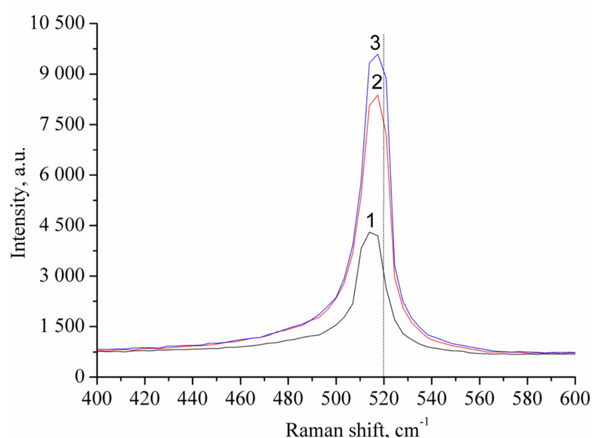


Figure 6 – Raman spectra of Por-Si samples grown at different conditions:
1 – J = 1 mA/cm$^2$, t = 20 min .;
2 – J = 15 mA/cm$^2$, t = 2 min .;
3 – J = 25 mA/cm$^2$, t = 1 min

## 4 Conclusions

In this work the dependence of structural and photoluminescent properties of PS layers on technological parameters of its fabrication were studied. Analysis of PS layers with the same thickness showed that increasing the etching time leads to a more advanced surface morphology and increased porosity. The films produced during the etching 1-2 minutes characterized by mean square roughness $S_q$ = 1.63-1.85 nm and for specimen obtained within 20 minutes $S_q$ = 2.96 nm; the characteristic size of the heterogeneity on the surface of the PS films increased from 4.2 nm to 8.4 nm. Scanning electron microscopy confirmed that the concentration distribution of pores was uniformly over the surface, and pore size ranges from 7 nm to 9 nm.

Applying Raman measurements, crystallite size was found to be 3.8 – 6.6nm; with increasing etching time from 1 minute to 20 minutes crystallite size was increased. It was found that the photoluminescence intensity is higher in samples with crystallite size of 3.8 nm, and the maximum was shifted to shorter wavelengths and was localized at 650 nm.

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