

# Morphology and FT IR spectra of porous silicon

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The morphology and chemical bonds of p-type and n-type porous Si was compared. The surface of n-type sample is smooth, homogenous without any features. The surface of p-type sample reveals micrometer-sized islands. FTIR investigation reveals various distribution of  $\text{SiO}_x\text{H}_y$  complexes in both p- and n-type samples. From the conditions leading to porous silicon layer formation (the presence of holes) we suggest both  $\text{SiO}_x\text{H}_y$  and  $\text{SiF}_x\text{H}_y$  complexes in the layer.

**Key words:** porous silicon, nanoparticles, anodic etching, morphology

## 1 Introduction

Porous silicon is a semiconductor with a high surface-to-volume ratio produced by electrochemical anodization or chemical etching of silicon. It is a highly Si-based absorbent without anti-reflection coatings with optimal electrical and optical properties. To manufacture this structure, many methods have been developed [1-5]. Improvement of the properties of porous silicon can be accomplished by passivation mechanism. This eliminates defect states, increases the conversion efficiency and creates a stable layer. Oxidation of porous silicon is one of the most suitable passivation procedures [6]. This procedure also creates Si nanocrystallites covered by  $\text{SiO}_x$  layer [7,8]. The size and structure of nanoparticles is crucial for formation of layers with desired electrical and optical properties. Porous Si layer is created by anodic etching of Si in an electrochemical cell [9]. The electric field between the cathode (platinum) and anode (silicon) drives holes to the Si/electrolyte interface. Silicon strongly reacts with HF leading to dissolution of Si. Holes in P-type Si cause etching of the Si layer. Since holes are minority carriers in N-type Si, they do not contribute to Si dissolution [10].

We compare the morphology and infrared spectra of p-type and n-type samples and analyse the processes leading to the formation of various structures by means of Fourier transform infrared spectroscopy and scanning electron microscopy.

## 2 Experimental part

Porous silicon was prepared by electrochemical etching in a teflon cell. Silicon surfaces of P-type boron doped (100) c-Si with resistivity 8-12  $\Omega\text{ cm}$  and thickness 600

- 650 nm and n-type antimony doped (100) c-Si with resistivity 0.02  $\Omega\text{ cm}$  of thickness 500 nm in HF vapors were cleaned, immersed in water and pure  $\text{CH}_3\text{OH}$  (methanol). The silicon wafer creates the anode and a platinum cathode as a mesh is located in the cell cavity. The etching solution 48% wt HF solution in pure methanol (1:2) is added to the cell cavity for 10 min. The etching current was 50 mA. Finally they were annealed in a chamber with pressure 150 bar, 15 wt%  $\text{N}_2$ , at temperature 250  $^\circ\text{C}$  for 30 min.

Samples were analysed by optical microscope Leica DM 2700 with camera DMC 2900 and scanning electron microscope (SEM) EVO LS 15 (ZEISS) with the accelerating voltage of 3 kV. Simultaneous EDX line analysis was performed with AMETEK (EDAX) EDS Element Silicon Drift Detector. The time of spectrum collection was 200 s with the energy range 0.160 to 8 kV. The samples were analysed by FT-IR absorption spectroscopy (ATR-diamond technique) using Digilab Excalibur FTS 3000MX spectrometer in the range 4000 - 600  $\text{cm}^{-1}$ , resolution of 4  $\text{cm}^{-1}$  and as much as 60 Co-added scans for obtaining information on different types of bonding in the structures.

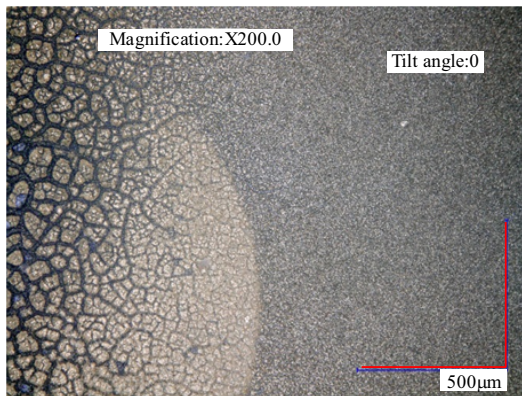
### 2.1 Optical and electron microscopy

Investigation of the n-type sample with optical and scanning electron microscope reveals smooth, homogeneous surface without any features.

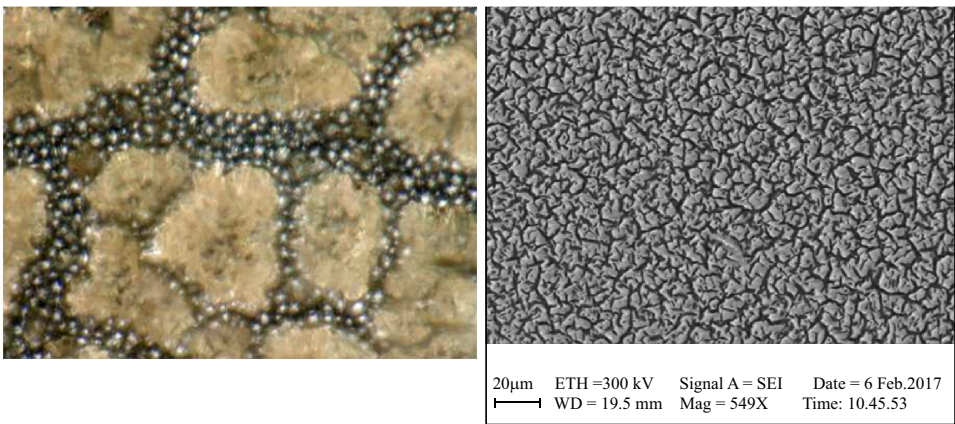
Investigation of p-type sample with optical microscope reveals three different areas black, white and crossbanding. Morphologies of these areas are different (Fig. 1).

The black area under light microscope reveals an almost smooth morphology (Fig. 2, left). The electron microscope reveals a continuous, unbroken surface consist-

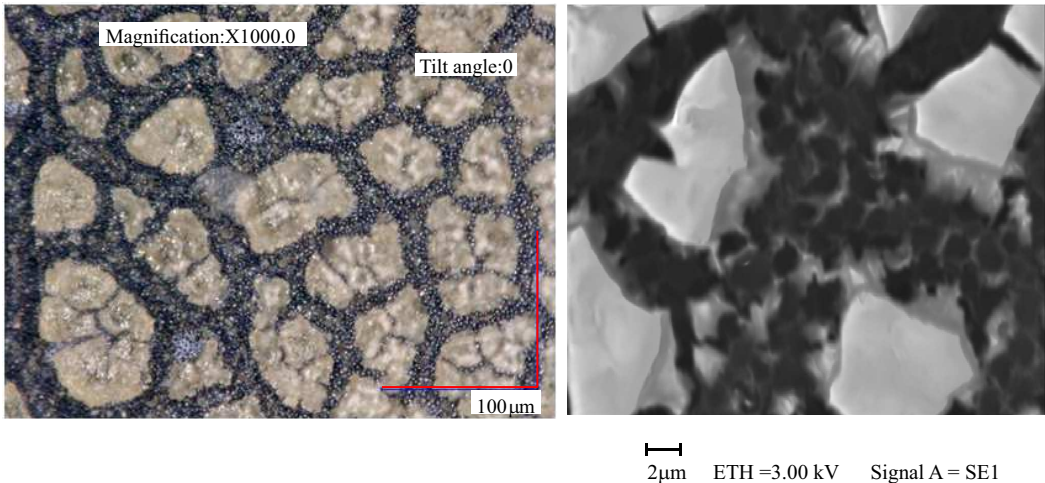
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**Fig. 1.** Image of three areas of p- type sample taken by optical microscopy



**Fig. 2.** Image of black area of p- type sample taken by optical microscopy (left) and electron microscopy (right)



**Fig. 3.** Image of white area of p- type sample taken by optical microscopy ( left ) and electron microscopy (right)

ing of a large amount of tiny, interconnected islands with small cracks between them (Fig. 2, right).

The white area under light microscope reveals isolated islands with a size of 5 - 10 micrometers (Fig. 3, left). Electron microscope reveals islands with sharp edges. A rough surface is observed between the islands (Fig. 3, right). The crossbanding area shows sporadically isolated islands.

**2.2 FT IR (ATR mode) description of the samples**

In all investigated samples in the range 750 - 1300  $\text{cm}^{-1}$  four absorption bands are seen: broad absorption from 790  $\text{cm}^{-1}$  to 900  $\text{cm}^{-1}$ , unclear absorption band at 905  $\text{cm}^{-1}$  and 936  $\text{cm}^{-1}$  and broad absorption from 980  $\text{cm}^{-1}$  to 1240  $\text{cm}^{-1}$  (Fig. 4, Table 1).

Deconvolution was performed of absorption from 790- 900  $\text{cm}^{-1}$  of all samples (Fig. 5). Peak positions after deconvolution for all samples are shown Tab. 2.

**Table 1.** FT IR vibrational frequencies for absorption bands in the range 750–1300 cm<sup>-1</sup>

Absorption band	Wavenumber (cm <sup>-1</sup> )	Reference
HSi(O)OSi(O)H	835	[11]
Si <sub>2</sub> F <sub>6</sub> O	839	[12]
Si-H <sub>3</sub>	870	[13]
HSi(O) <sub>2</sub> OSi(O) <sub>2</sub> H	868	[11]
HSiH	901	[14]
		[15]
Si-H	905	[16]
H <sub>2</sub> Si(O)...SiH <sub>2</sub>	938	[11]
H <sub>2</sub> Si(O)...SiH <sub>2</sub>		
H <sub>2</sub> Si(O) <sub>2</sub> ...SiH <sub>2</sub>	976	[11]
H <sub>2</sub> Si(O) <sub>2</sub> ...Si(O) <sub>2</sub> H <sub>2</sub>		
SiF <sub>4</sub>	1031	[17]
HSi(O)OSiH	1038	[14]
H <sub>2</sub> Si(O)—2 dots SiH <sub>2</sub>	1125	[11]
SiO <sub>4</sub>	1150	[18]
		[19]
Si-(CH <sub>3</sub> ) <sub>n</sub>	1260, 800	[20]

**Table 2.** Peak position of absorption 790-900 cm<sup>-1</sup> after deconvolution

Samples (type)	Fit peak 1	Fit peak 2
n	830	865
p, white area	834	872
p, crossbanding area	836	869
p, black	836	874

**Table 3.** Peak position after deconvolution of absorption 950–1250 cm<sup>-1</sup>

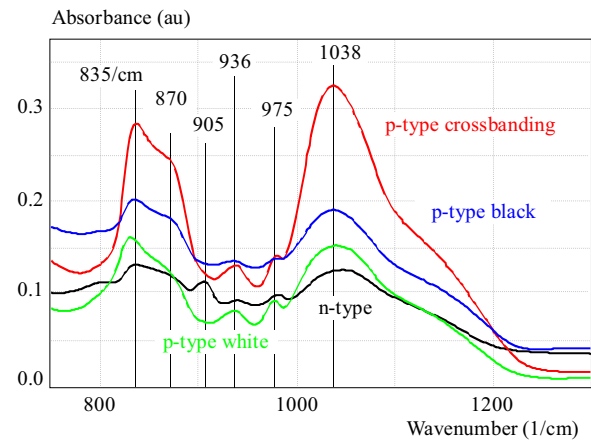
Samples (type)	Fit peak 1	Fit peak 2
n	1042	1142
p, white area	1033	1120
p, crossbanding area	1033	1121
p, black area	1035	1147

The amplitude and full width at half maximum (FWHM) analysis of the peak around 835 cm<sup>-1</sup> for black and white areas of p-type sample shows very similar parameters (slight difference in SiO<sub>x</sub>H<sub>y</sub>). A similar effect is observed from the analysis of the second peak around 870 cm<sup>-1</sup>. The crossbanding area shows the highest amplitude with lowest FWHM.

Deconvolution was conducted of absorption from 950–1250 cm<sup>-1</sup> of all samples (Fig. 6). Peak positions after deconvolution for all samples are shown Tab. 3.

The amplitude and FWHM of the peak around 1026 cm<sup>-1</sup> for black and white areas of p-type sample shows the presence of different SiO<sub>x</sub>H<sub>y</sub> complexes. We cannot

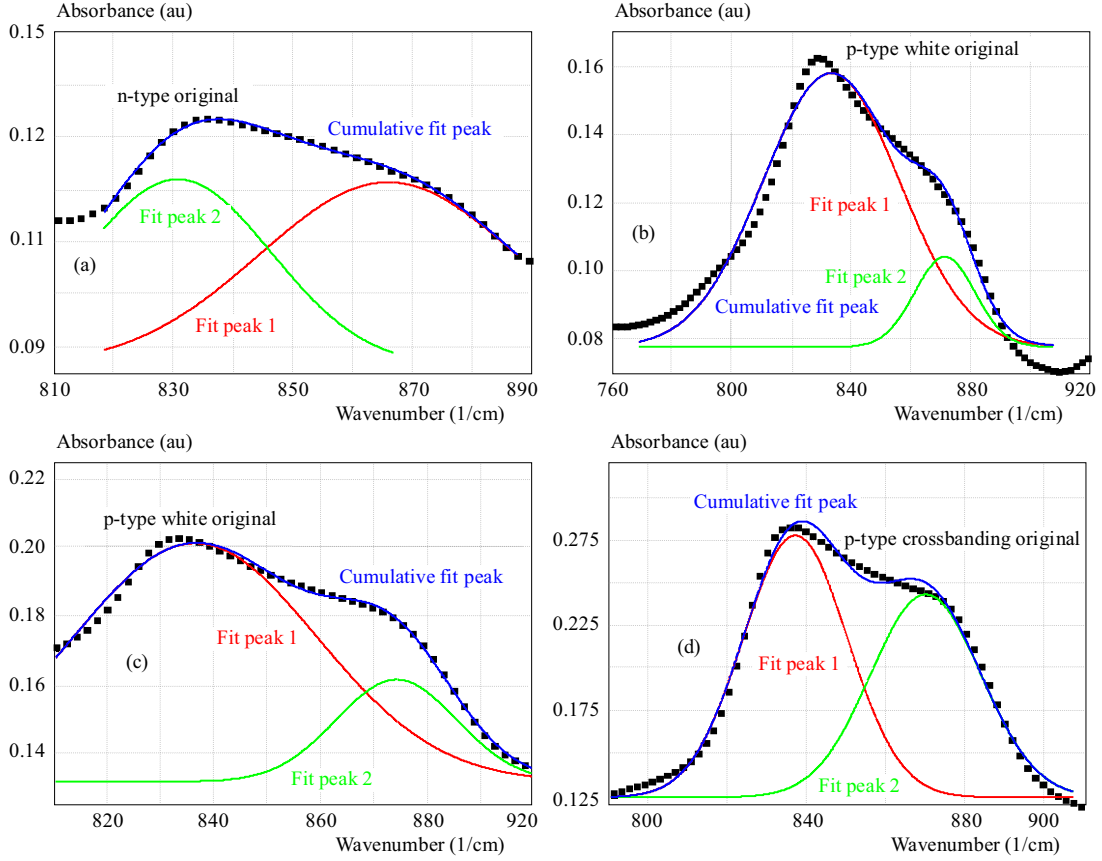
rule out the presence of another band in the silicon layer such as Si-CH<sub>3</sub>.

**Fig. 4.** FTIR spectra of n- and p-type porous silicon structures in the range 750–1300 cm<sup>-1</sup>

### 3 Discussion

Porous silicon is described as a silicon layer with nanocrystallines embedded. Its properties are influenced by many factors such as etching parameters, crystal orientation, dopant type, current density, etching solution and time. Electron microscopy confirmed various structures of silicon layer. It reveals that n-type sample has a smooth, homogeneous surface without any features at the level of nanometers. Only this sample reveals the presence of absorption band assigned to Si-H bonds (905 cm<sup>-1</sup>) and absorption about 2100 cm<sup>-1</sup> assigned to SiH<sub>n</sub>,  $n = 1, 2, 3$ . In addition, presence of SiO<sub>x</sub>H<sub>y</sub> complexes can be observed. The black area of p-type sample shows a continuous, unbroken surface consisting of large amount of tiny, interconnected islands with small cracks between them. Unlike n-type sample, the p-type sample does not exhibit an absorption band at 905 cm<sup>-1</sup>. Deconvolution of absorption in the range 790–900 cm<sup>-1</sup> shows a shift of absorption to higher wavenumbers of the p-type sample. This observation can be explained by formation of different SiO<sub>x</sub>H<sub>y</sub> complexes in the p-type sample. These two samples (p- and n-type) show the presence of SiO<sub>4</sub> absorption. FWHM of absorption reflects conditions prevailing in the silicon oxide layer such as disorder, mechanical stress, environmental effect, bond angle distortion of bonds or etching process. Compressive stress arising at Si/SiO<sub>2</sub> interfaces is responsible for the changes in IR spectra. From the results of the central force model it is evident that compressive stress causes a decrease in the average tetrahedral SiOSi bond angle whose normal average value is 144 °C, [21]. Velde et County [22] investigated high-pressure infrared spectra of amorphous SiO<sub>2</sub>. They suggest that the absorption peak around 1090 cm<sup>-1</sup> is due to compression of the structures and not

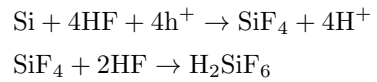




**Fig. 5.** Results of the analysis of the absorption bands in terms of two gaussian components for p- and n- type samples

due to changes in the bonding of the Si-O. They conclude the presence of at least two arrangements of  $\text{SiO}_4$  tetrahedrons. These units with Si as a central tetrahedral atom can be bridged through O atoms. The absorption peak at around  $1090 \text{ cm}^{-1}$  is attributed to five tetrahedral units with four bridging O atoms. Furukawa *et al* [23] investigated the peak position in  $\text{SiO}_2$  thin films prepared by sputtering-type electron resonance methods. They found that at a certain flow rate of oxygen (3-6 sccm) the peak position was  $1075 \text{ cm}^{-1}$ , but FWHM decreases with an increase of the flow rate of oxygen. During preparation of Si/ $\text{SiO}_2$  a thin layer at high temperature goes through phase separation [24]. This process results in formation of Si nanoclusters in  $\text{SiO}_2$  films. A shift was observed of the absorption peak from  $1025 \text{ cm}^{-1}$  to  $1078 \text{ cm}^{-1}$  with increasing annealing temperature from  $900^\circ\text{C}$  to  $1100^\circ\text{C}$ . Transmission electron microscopy and X-ray diffraction confirm the formation of crystalline Si precipitates within the amorphous  $\text{SiO}_2$  matrix during annealing. From photoluminescence spectra, Ding *et al* [25] suggest the presence of nc-Si/ $\text{SiO}_2$  interface assigned to absorption at  $1083 \text{ cm}^{-1}$ . Lisovskii *et al* [26] investigated the structure of  $\text{SiO}_2$  thin and ultrathin films before and after bombardment with  $^{40}\text{Ar}$  ions of  $2.7 \text{ keV}$ . Deconvolution of Si-O band revealed an absorption band around  $1012 \text{ cm}^{-1}$  and  $1038 \text{ cm}^{-1}$ . They suggest a modified layer structure with a cluster of  $\text{Si-O}_x\text{-Si}_{4-x}$  where  $0 \leq x \leq 4$  depending on the depth.

The formation of nanocrystalline Si layer by Lai *et al* [10] was described



This dissolution of the silicon layer can lead to formation of  $\text{SiF}_x\text{O}_y$  complexes ( $\text{SiF}_3\text{H}$ ,  $\text{SiF}_2\text{H}_2$ ,  $\text{SiFH}_3$ ), [28,29]. The presence of these complexes can influence the morphology of the silicon oxide layer. Optical microscopy, electron microscopy and infrared spectroscopy reveal different morphologies and formation of bonds and complexes in p-type and n-type samples. Because the holes influence dissolution of Si and formation of  $\text{SiF}_x\text{O}_y$  complexes, we suggest that islands of 4pz samples consist of both  $\text{SiO}_x\text{H}_y$  and  $\text{SiF}_x\text{O}_y$  complexes.

#### 4 Conclusion

We compared the morphology and chemical bonds in p-type and n-type silicon samples. We found that the surface of n-type sample is smooth, homogeneous without any features. The surface of p-type sample exhibits micrometer-sized islands. FTIR investigation reveals various distribution of  $\text{SiO}_x\text{H}_y$  complexes in both p- and n-type samples. From conditions leading to silicon layer for-

mation (presence of holes) we suggest both  $\text{SiO}_x\text{H}_y$  and  $\text{SiF}_x\text{O}_y$  complexes in the layer.

### Acknowledgements

This work was partly financially supported by APVV project No. APVV-15-0152 and VEGA No. VEGA-2/0076/15. We also thank to Mr Peter Zitto a Mrs Silvia Bacova for technical support.

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Received 23 April 2017