

FABRICATION INFLUENCE ON THE SURFACE MORPHOLOGY AND STRUCTURE OF VAPOUR ETCHED POROUS SILICON

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The structure and properties of porous silicon produced applying vapour-phase chemical etching of Si in HF:HNO₃ acid mixture are analysed. Experimental layers of different porosity with pores of different size and shape corresponding to different active surface areas, were formed by varying the etching parameters. The fabricated structures were investigated using the X-ray diffractometry (XRD), Raman spectroscopy (RS), infrared spectroscopy (FTIR) and photoluminescence spectrometry (PL) methods. SEM imaging was used for the visualization of the produced structures. The refractive index of the experimental layers was evaluated by optical ellipsometry measurements and used for layer porosity estimation. The crystallite size in the fabricated porous structures was estimated taking into account the presence of porous (p-Si), crystalline (c-Si) and amorphous (a-Si) structures in the experimental layers. The size of crystallites in the porous Si layers was found to vary from 3.1 nm to 4.3 nm, and layer porosity varied from 61.4 to 86.7% in different samples.

Fabrication of mesoporous silicon structures containing nanosized crystallites, achieved by controlling vapour-phase chemical etching parameters, is discussed on the basis of the obtained results.

Keywords: vapour-phase etching, porous Si, nanocrystalline, mesoporous structure

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1. Introduction

Porous silicon in various geometries and morphologies can be used for novel optical elements by combining theoretical insights with a suitable porous structure depending on the technological parameters of fabrication methods and some pre- and post-processing of the silicon. Usually, porous silicon is produced by electrochemical etching of Si target; however, in some cases chemical etching of Si in the vapour-phase of HF:HNO₃ acid mixture is applied for the fabrication of unique porous silicon structures with a characteristic morphology [1–8]. Applying vapour-phase chemical etching of Si, it is possible to produce mesoporous and nanoporous silicon structures with embedded nanoclusters containing

luminescent dot-like Si particles or to enhance the active surface area. The morphology and luminescence of nanoporous Si are dependent on the bulk properties (especially Si doping) and technological parameters of etching. The formation mechanism of a porous structure is explained in general, but there are still some details remaining, such as the impact of fabrication parameters on the properties of nanoporous structures, which require further investigation.

The aim of the present work was to produce different porous silicon layers on silicon substrate, using the simple vapour-phase chemical etching method, and to investigate the influence of technological parameters on the structure formation, morphology and luminescence properties of the fabricated porous silicon structures.

2. Instruments and methods

One-side polished p-type silicon (111) samples were used as a target for the production of a porous silicon skeleton. Samples with a contact surface area of approximately 1 cm² (smaller than the total Si wafer area) were placed on the top of a teflon cell at a distance of 10 mm from the surface of a liquid mixture of the acids HF and HNO₃. Chemical etching was performed in the vapour-phase of the acids mixture at a temperature of 20 °C. In order to keep the same temperature of acids during the long-term etching process, the teflon cell was immersed into a water bath equipped with a Pt thermometer connected through the regulator to the heating element (Fig. 1).

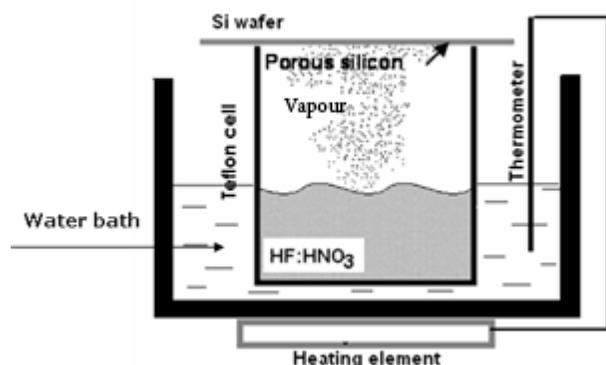


Fig. 1. Experimental set-up for the chemical etching of Si in vapour phase of HF : HNO₃ acids mixture.

Two series of porous silicon samples were produced: (i) varying concentrations of acids in the HF : HNO₃ mixture (1 : 1, 1 : 2 and 1 : 6) and keeping the same etching time of 24 h, and (ii) keeping the same concentration of HF : HNO₃ acids as 4 : 1 and changing the etching time (24, 48 and 60 h). The main fabrication parameters and some initial characteristics of the experimental structures are provided in Table 1.

A rapid visual test to ensure that porous Si structures had been produced was performed by irradiating experimental samples with a UV lamp (wavelength 254 nm) in a Min UVIS Desaga spectrometer. All experimental samples were highly luminescent, indicating typical porous Si structures. A porous structure of the experimental samples was visible in the images obtained using a FEI QUANTA 200FEG scanning electron microscope (SEM).

Assuming that a porous Si layer is thicker than the depth of the individual pores, layer thickness was evaluated using an MII-4 interference microscope. Due to the inhomogeneity of the fabricated layers, the height of the interference step corresponding to the layer thickness was measured several times in different positions. Bruggeman's model was applied for the calculation of sample porosity [9]:

$$P = 1 - \left[\frac{(1 - n_{ps}^2)(n_{si}^2 + 2 \cdot n_{ps}^2)}{3 \cdot n_{ps}^2 \cdot (1 - n_{si}^2)} \right] \cdot 100\% , \quad (1)$$

where n_{si} is the refractive index of silicon and n_{ps} is the refractive index of a porous Si layer, evaluated from ellipsometric measurements using a Gaertner L117 laser ellipsometer operating with a He-Ne laser (exciting wavelength 632.8 nm).

The chemical bonding structure of porous Si layers was analysed using a Raman scattering spectrometer (Yvon Jobin System) and an FT-IR spectrometer (Nicolet 5700, equipped with a 10-degree Specular Reflectance Accessory). The crystalline structure of the produced porous Si layers was analysed, and the size of crystallites was estimated from XRD spectra obtained using a DRON-6 X-ray diffractometer operating at 35 kV and 20 mA and equipped with a single crystal graphite flat monochromator for transmitting only a narrow Cu K_{α} wavelength ($\lambda = 0.15405$ nm). Diffraction patterns were recorded in a scanning mode with 0.02° steps of 2 θ and the counting time of 0.5 s per step. Qualitative phase identification was performed using the PDF-2 data base. Raman spectra were used to estimate crystallite size as well. A permanent Ar laser ILA 120 beam (wavelength 488 nm, incidence angle 45°, beam modulation frequency 130 Hz, maximum excitation power 100 mW) was used for photoluminescence excitation in experimental samples at different temperatures. The photoluminescence of samples was detected with a GaAs detector supported with a photomultiplier FEU-157 and analysed in an MDP12 monochromator. Photoluminescence spectra were used for the evaluation of porous Si structures.

3. Results and discussion

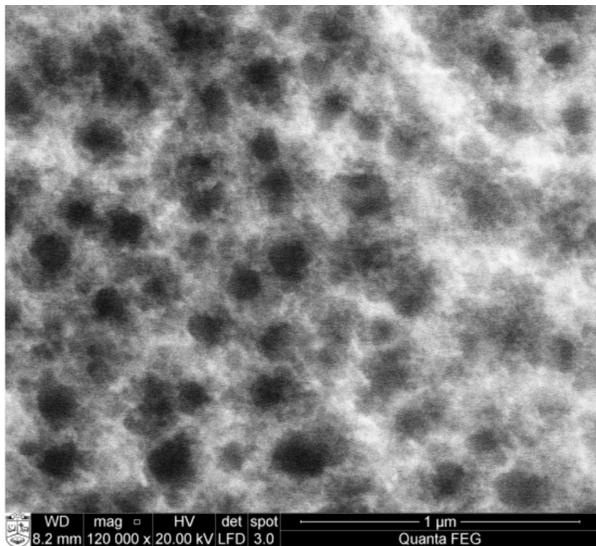
Porous silicon structures with pores of different size and shape were produced varying the vapour-phase chemical etching process parameters. A certain

correlation was found between the thickness and porosity of the experimental layers and acid concentration in a mixture. An increased HNO_3 concentration in a mixture during the same etching time corresponded to the formation of thinner porous Si layers with a lower porosity (Table 1).

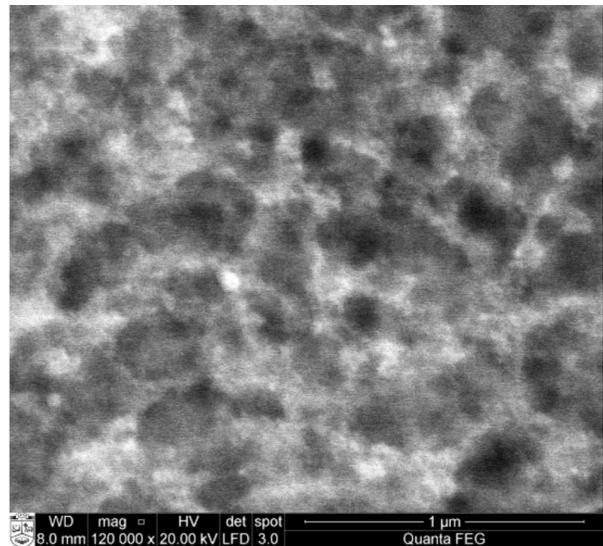
An increased HF concentration in a mixture of acids led to a lower porosity of layers if the sample etching time remained the same, as it could be assumed from SEM images of sample N11 (Fig. 2a) and sample N5 (Fig. 2b), as well as from the calculated values of porosity, presented in Table 1.

Table 1. Main fabrication parameters and characteristics of experimental porous silicon structures

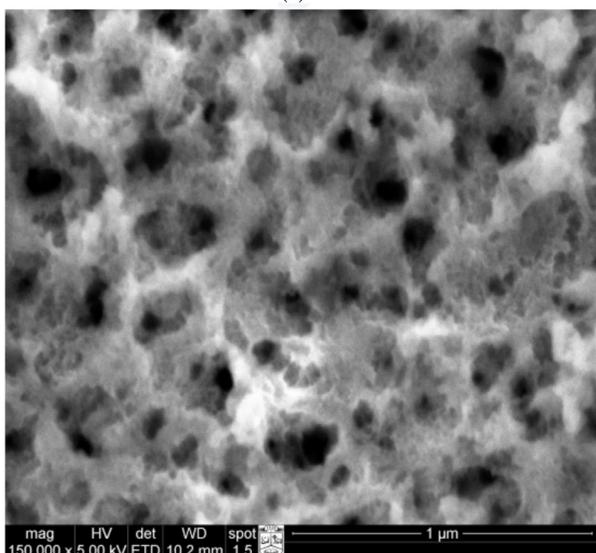
Series	Samples	HF : HNO_3	Etching time, h	Porous layer thickness, μm	Refractive index	Porosity, %
I	N11	1 : 6	24	4.201	1.21	83.6
	N10	1 : 2	24	2.767	1.32	75.3
	N8	1 : 1	24	2.103	1.50	61.4
II	N5	4 : 1	24	2.013	1.43	66.8
	N20	4 : 1	48	3.934	1.21	83.6
	N4	4 : 1	60	4.851	1.17	86.7



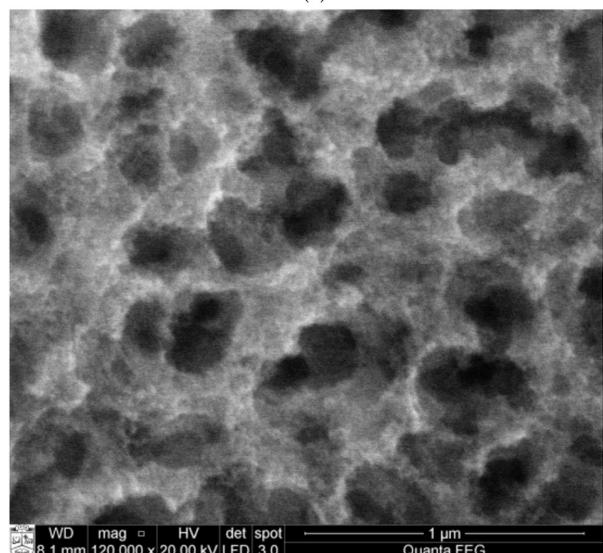
(a)



(b)



(c)



(d)

Fig. 2. SEM images (top view) of fabricated porous Si layers: sample N11 (magn. $\times 120\,000$) (a); sample N5 (magn. $\times 120\,000$) (b); sample N20 (magn. $\times 150\,000$) (c); sample N4 (magn. $\times 120\,000$) (d).

Keeping the same ratio 4 : 1 of the HF : HNO₃ acids in a mixture and increasing the etching time, thicker porous Si layers of higher porosity and a larger active surface area were produced (samples N20, N4 in Fig. 2). These samples were characterized by pores of different size and shape non-uniformly distributed within a porous layer. The same 83.6% porosity was found in samples N11 (Fig. 2(a)) and N20 (Fig. 2(c)) produced in different etching conditions. It was possibly due to the inhomogeneity of porous layers containing a variety of freely distributed pores.

As a result of anisotropic etching, the interface between the Si substrate and the porous layer was quite rough, and formation of a pyramidal structure was observed in SEM images (Fig. 3).

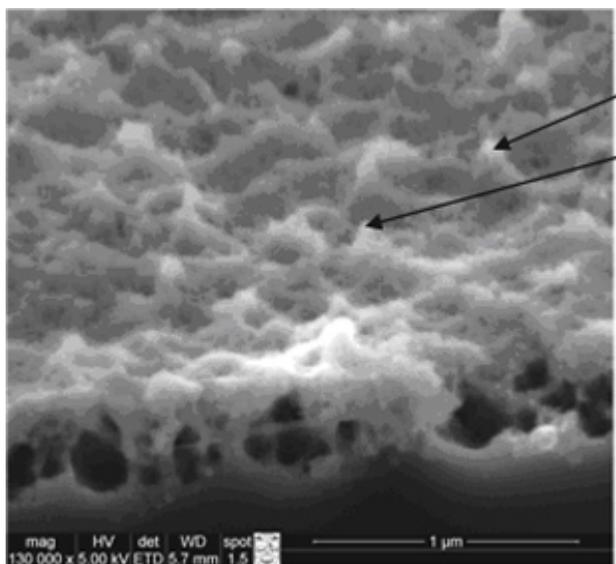


Fig. 3. SEM image of a sample N20 (tilted by 45°, magn. ×130 000) with indicated pyramidal texture.

The bonding structure in porous Si layers depended on the etching conditions – HF content in the HF : HNO₃ acid mixture and the etching time and on the pore growth mechanisms [4, 5]. It was analysed using the results of IR spectroscopy. Peaks corresponding to Si–H bending (2248–2250 cm⁻¹), Si–H_n bending (578–638 cm⁻¹), Si–O–Si asymmetric stretching (1029–1104 cm⁻¹), Si=O stretching (1137–1151 cm⁻¹) and a doublet of Si–O–H bending (880 and 840 cm⁻¹) bonds that are usually observed in the porous silicon structure were present in all samples. The relative intensity of competing Si–O–Si and Si–H_n peaks was decreasing with in-

creasing the etching time (Fig. 4, sample N5 and Fig. 4, sample N4) due to the etching of inner surfaces in porous silicon structures. Formation of Si–O–Si and the Si–H_n bonds in the etched samples depends on the ratio of HF : HNO₃ acids as well. The highest peak intensities were found in samples N11 (Fig. 4) etched at the lowest HF content in a mixture (HF : HNO₃ = 1 : 6), corresponding to the growth of small diameter pores into the depth. The FTIR spectrum of N8 sample, produced at the acid ratio 1 : 1, is provided in Fig. 4 for a comparison of the results.

X-ray diffraction measurements were used to confirm the presence of Si crystallite clusters in the fabricated porous silicon structures as indicated in SEM images. Segments of XRD spectra, corresponding to porous structures produced in different fabrication conditions, are presented in Fig. 5.

The X-ray diffraction patterns show two well-resolved peaks, corresponding to the lattice parameter of the porous Si (400) layer (left) and the Si (100) substrate (right), indicating that the porous Si has the same crystalline structure as the bulk Si, but with larger lattice parameters [10, 11]. The intensity of the porous Si peak (400) was increasing with the etching time and porosity of layers. The angular distance $\Delta\varpi$ between the Bragg peaks of porous silicon and silicon substrate is related to the lattice mismatch $\Delta a/a$:

$$\frac{\Delta a}{a} = -\frac{\Delta\varpi}{\tan\varpi_B}, \quad (2)$$

where ϖ_B is the silicon substrate peak position [9]. The lattice mismatch $\Delta a/a$, given by peak separation, increases with porosity and is about $2.5 \cdot 10^{-3}$. Small lattice distortions in crystalline planes are increasing when the thickness of the porous Si layer increases, and depend on the layer formation parameters. It is well known [6, 12] that the XRD peak width depends on the average crystallite size which may be evaluated using Scherrer's formula:

$$d = \frac{k \cdot \lambda}{\beta \cdot \cos\theta}, \quad (3)$$

where d is a crystallite size, λ is X-ray wavelength, β is FWHM of peak, θ is Bragg angle, k is Scherrer constant, which depends on the crystallite shape and diffraction line index. Evaluated crystallite size (Table 2) varied in the range of 3.1–3.8 nm and was dependent on vapour-phase etching parameters.

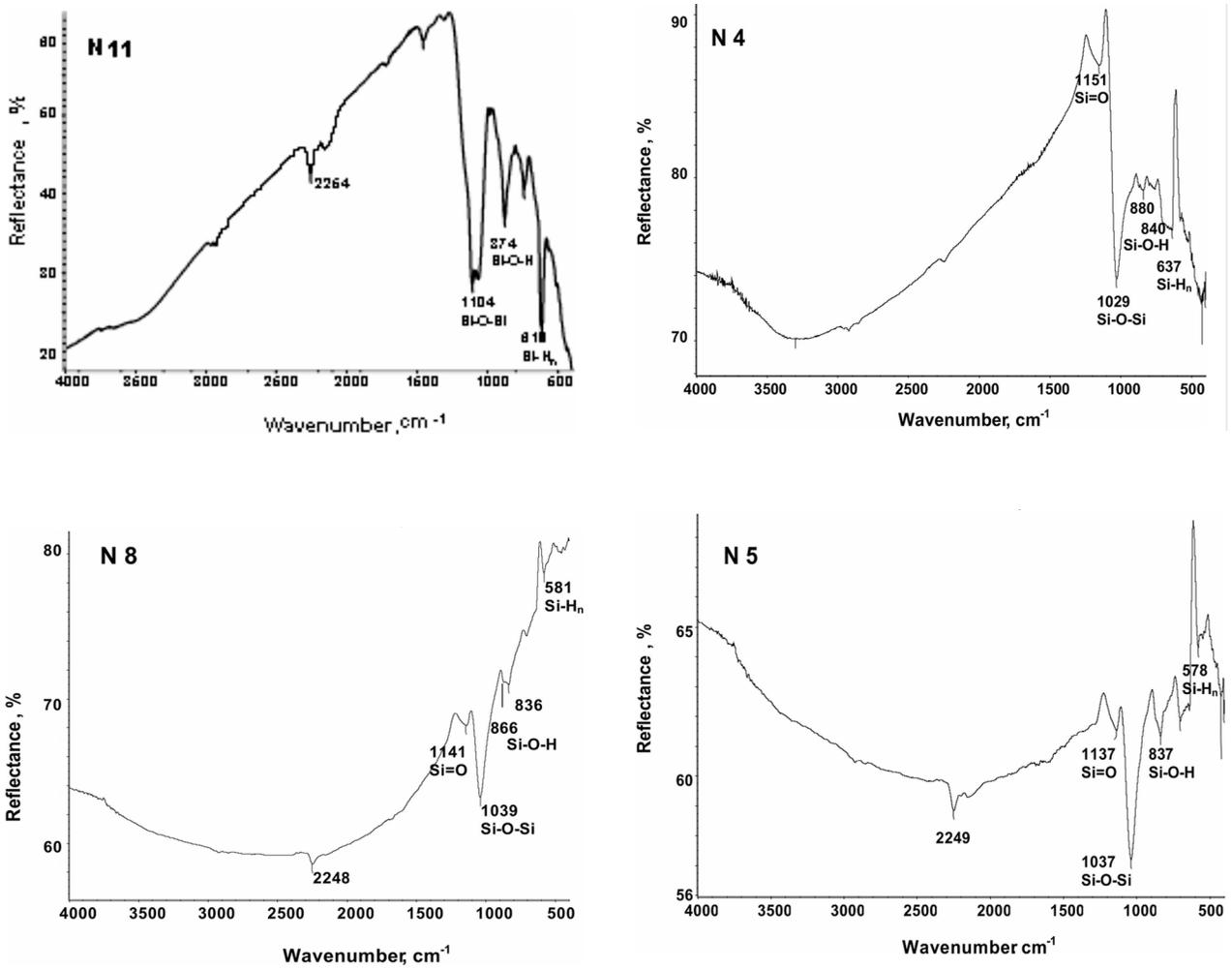


Fig. 4. FTIR spectra of porous Si structures produced by varying fabrication parameters. Fabrication parameters of samples are presented in Table 1.

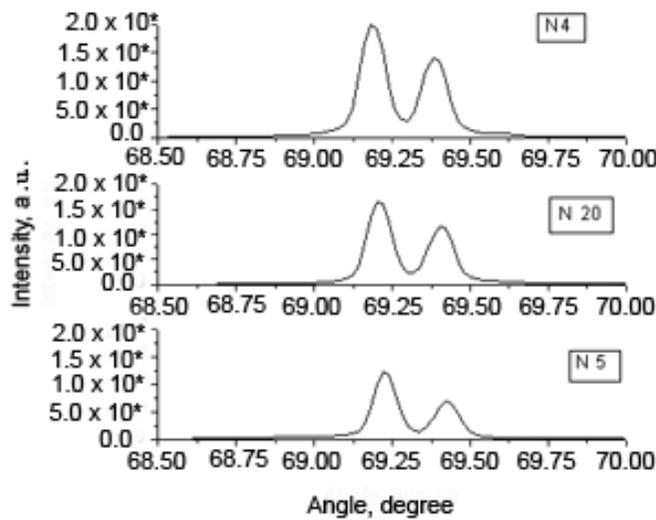


Fig. 5. XRD spectra of samples fabricated keeping the same 4 : 1 HF : HNO₃ concentration in the mixture but using different etching time.

A decrease in the average crystallite size indicated an increase in porosity. Clusters of small-sized crystallites were characteristic of both mesoporous (pore size >50 nm) and nanoporous silicon.

The non-destructive Raman scattering method provides additional information about the structure of fabricated porous silicon layers. The Raman spectra can be decomposed into several bands corresponding to different organized structures. Information about nanocrystallite size can be obtained from the corresponding peak shape and peak posi-

tion. The finite size effects, which destroy the full translational symmetry of the material, result in a low-frequency asymmetric broadening and red shift of the Raman band.

The fitting of the Raman bands was achieved by the Gaussian convolution of Raman spectra of the samples (Fig. 6).

The performed procedure resulted in identification of three main peaks in Si structures, corresponding to crystalline (c-Si, peak 3), amorphous (a-Si, peak 1) and porous (p-Si, peak 2) silicon. Small

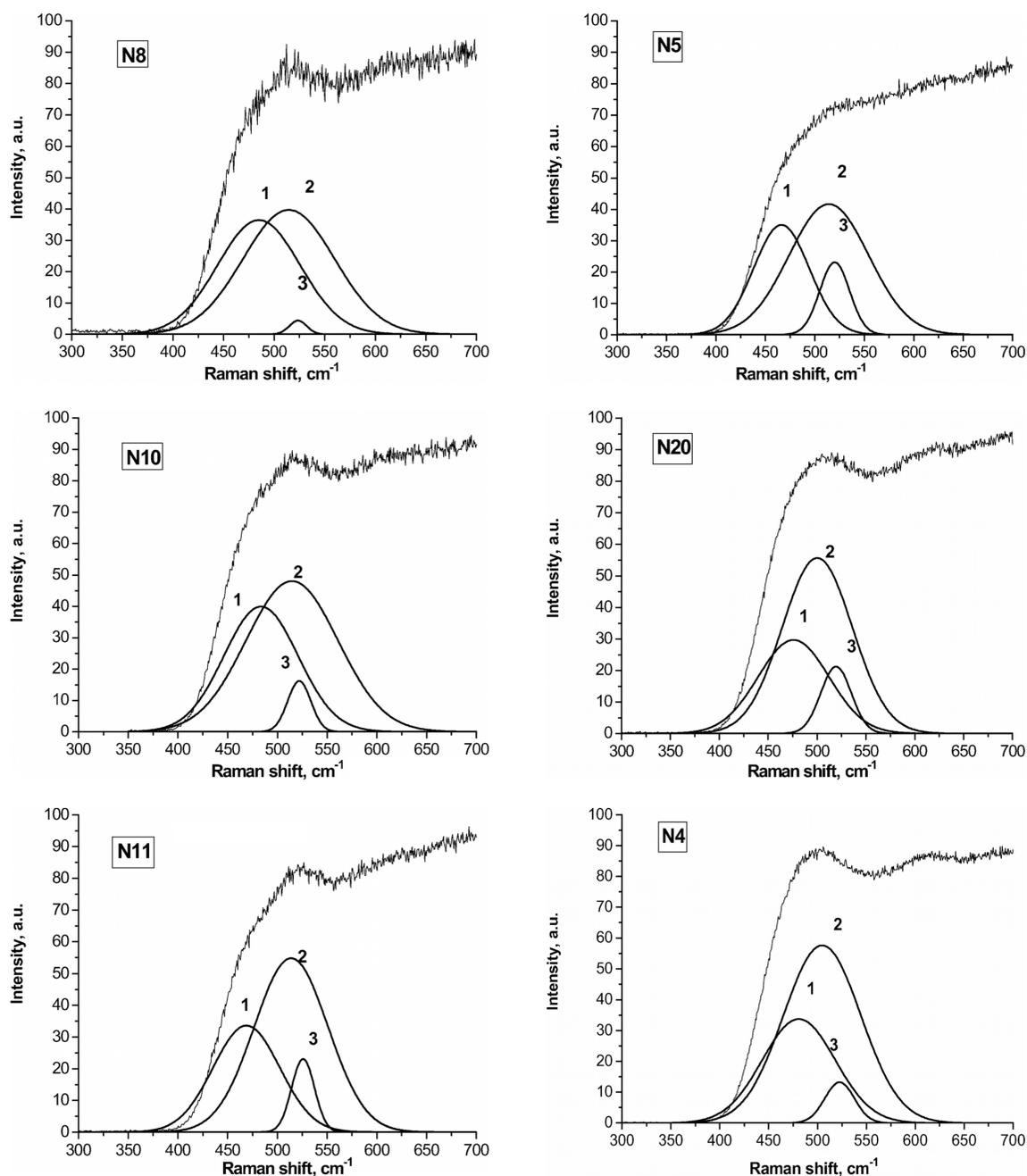


Fig. 6. Raman spectra of experimental samples including Gaussian convolution curves. Peak 1 corresponds to the amorphous Si, peak 2 corresponds to the porous Si, and peak 3 corresponds to the crystalline Si.

c-Si peaks (Fig. 6, peak 3) found at around 520 cm^{-1} , are associated with the longitudinal optical mode (LO) in the crystalline silicon. The observed Raman spectra broadening corresponding to the first split of the spectral peak at $466\text{--}489\text{ cm}^{-1}$ corresponded to the transverse optical (TO) mode in the amorphous silicon. The peak half width varied from 56 to 82 cm^{-1} . Both peaks (c-Si and a-Si) could be found in the initial non-etched samples. One more peak at $501\text{--}515\text{ cm}^{-1}$ with $71\text{--}92\text{ cm}^{-1}$ FWHM was found in the Raman spectra of the etched samples. Depending on the technological parameters of sample fabrication, it was shifted towards higher excitation energies, i. e. to a porous silicon peak. An intensive and broad-contour Raman peak with a typical continuum in the lower energy range corresponds to the formation of a nanoporous structure [13, 14]. It should be noted that the increasing tendency of the Raman spectra indicated existence of silicon oxides, which was confirmed by IR spectroscopy. A small shift of the Raman peak, corresponding to the porous Si as compared to the Raman peak of crystalline Si structure, indicates the presence of different-size crystallites and formation of the mesoporous structure. The increased concentration of HF in the acid mixture (Raman peak at 505 cm^{-1} for N4) clearly indicates a nanocrystalline structure. Information about nanocrystallite size can be obtained from the shape and peak position of the first-order Raman scattering band. Crystallite size was calculated according to the Cardona equation [15]:

$$d = \frac{2\pi(B/\Delta\omega)^{\frac{1}{2}}}{10} [\text{nm}], \quad (4)$$

where $B = 224\text{ cm}^{-1}$, $\Delta\omega$ is the Raman shift related to the c-Si peak. Crystallite size was found to vary between 3.1 and 4.0 nm (Table 2). An analysis of the spectra according to the model of phonon confinement in silicon nanocrystals [16] has indicated that

the nanocrystallites in nanoporous silicon are best approximated by spheres $2\text{--}4\text{ nm}$ in diameter.

The luminescent properties of nanostructured materials depend on the size and shape of nanoparticles. If the size of crystallites is $<5\text{ nm}$, luminescence is caused by the space quantification effects [17]. For reason, the PL spectra of porous Si samples were measured (Fig. 7), and a correlation among porous structure fabrication parameters, particle size and luminescence efficiency was investigated. Measurements were performed at four different temperatures: 3.6 , 35 , 77 and 300 K (room temperature) with the aim to assess the thermal aspect of luminescence in porous Si.

The PL peak position was found to depend on the temperature and fabrication parameters of porous structures. The intensity of photoluminescence spectra was comparable in all samples. Luminescence bands were not symmetric and had a higher intensity in the short-wave range. This feature corresponds to the relatively high content of nanocrystallites in the experimental samples. A small blue shift of the PL peak, indicating an increased porosity, was observed in porous Si samples at all temperatures when HNO_3 concentration in the HF : HNO_3 acid mixture or the etching time keeping a constant acid concentration ratio was increased. Samples of the same group produced at a relatively high HF concentration in the HF : HNO_3 acid mixture ($4 : 1$) indicated a PL peak shift towards lower energies at room temperature as compared to those measured at lower temperatures ($T \leq 77\text{ K}$) (Fig. 7) (samples 5, 20, 4). The increased concentration of HNO_3 in the mixture of acids and the constant etching time of samples were responsible for a significant shift of the PL peak to the higher energies at room temperature (Fig. 7, samples 8 and 11). The difference in the spectral positions of PL bands in porous silicon might also

Table 2. Crystallite size in porous Si structures

Sample	HF : HNO_3	Etching time, h	d, nm				Porosity, %
			XRD	Raman	PL, 300K	PL, 77 K	
N5	4 : 1	24	3.3	3.7	3.8	3.8	66.8
N20	4 : 1	48	3.2	3.5	3.7	3.6	83.6
N4	4 : 1	60	3.1	3.1	3.6	3.4	86.7
N11	1 : 6	24	3.6	3.5	3.4	3.6	83.6
N10	1 : 2	24	3.4	3.6	3.4	4.0	75.3
N8	1 : 1	24	3.8	4.0	3.5	4.3	61.4

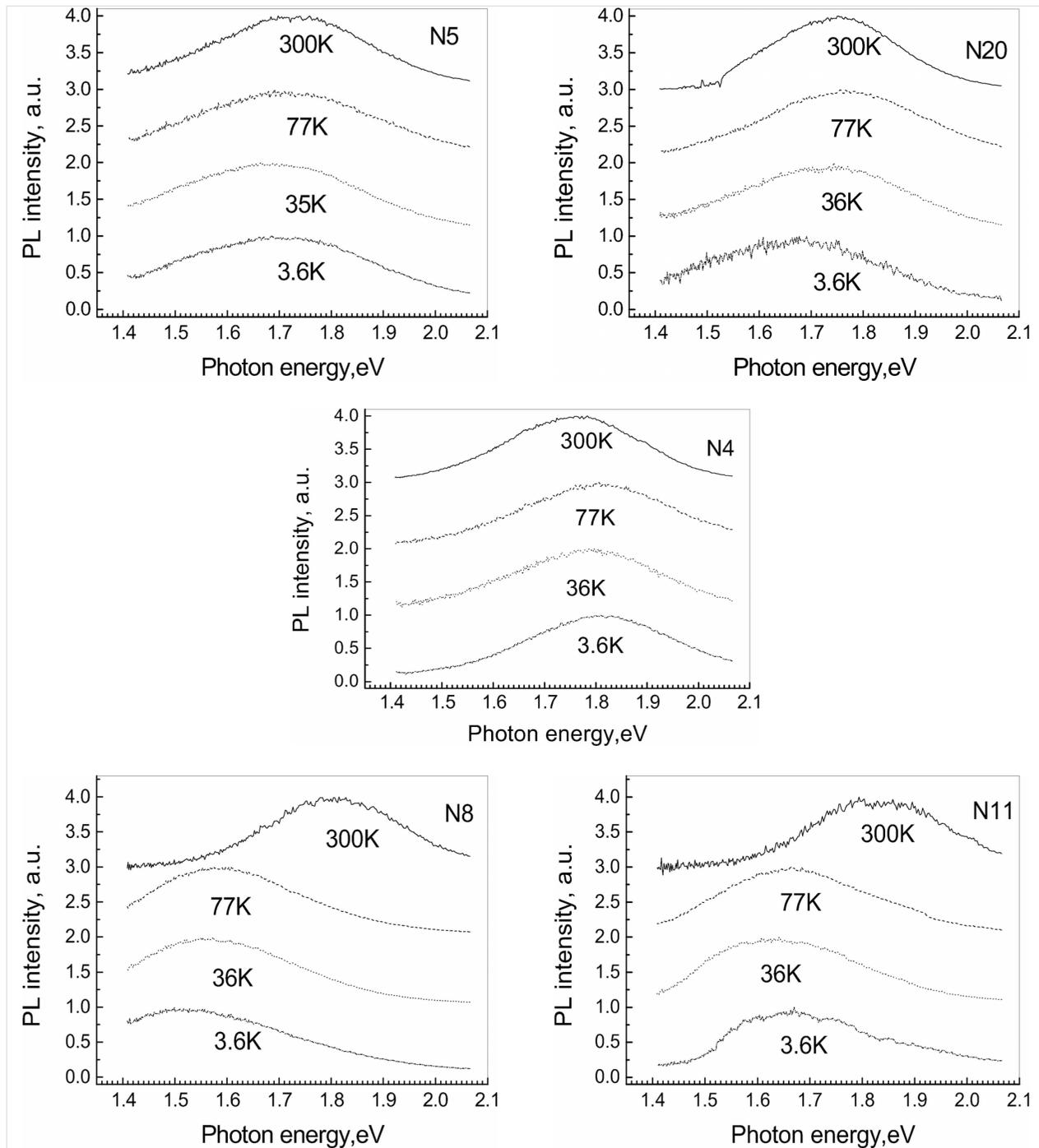


Fig. 7. Temperature-dependent PL spectra of porous structures produced by Si etching in the vapour phase of HF : HNO₃ acid mixture.

be caused by the different composition of silicon oxides on the Si surface where the corresponding radiation defects are localized [8, 11, 18]. The obtained differences could be explained by carrier recombination processes in nanocrystalline structures and phonon contribution to the radiant processes.

It is known [19] that the PL peak of crystalline Si corresponds to the energy of the forbidden gap. The PL peak at the quantum energy $h\nu = 1.13$ eV was estimated for crystalline Si targets used in the fabrication of experimental samples. According to [8], the PL peak has to be shifted towards higher energies by >0.4 eV in nanoporous structures.

Vapour-etched structures are characterized by crystallites of different size and shape, which additionally contribute to the shift of the spectrum band towards higher energies [20]. Therefore, a, slightly higher (0.5–0.7) eV “blue shift” of the peak in PL spectra, as compared with electrochemically produced samples, was observed in all study samples. Phonon spectra are dependent on the regularity of the micro structure and reflect the information about the pore distribution and density in a sample as well as about the size and shape of nanocrystallites in the structure [21]. Upon evaluating the shift of the PL peak, it was possible to calculate nanocrystallite size according to the empirical formula [15, 22, 23]:

$$E = E_0 + \frac{88.34}{d^{1.37}}, \quad (5)$$

where E_0 is the energy of the forbidden gap in crystalline Si, E is the energy corresponding to the peak position in PL spectrum, d is a size of nanocrystallite.

Crystallite size was calculated for two temperatures: 77 and 300 K, having in mind possible oxidation of the pore surface at room temperature. It is to point out, that crystallites of very small diameters should also exist, but they are not able to luminesce at the applied excitation wavelength (488 nm). Therefore, only mean diameter of luminescent crystallites was determined [23].

Results of crystallite size calculations using different methods are presented in Table 2.

Calculations have shown that the PL peak position is tightly related to the morphology of the study structure: a higher PL peak energy corresponds to the porous structure with clusters of 3.4–3.8 nm sized nanocrystallites. A low-intensity photoluminescence spectrum, the PL peak shifted towards lower energies and large-sized crystallites are the main characteristics of a mesoporous structure. At the size of crystallites $d > 4.0$ nm, the PL intensity increases very slowly due to luminescence defects caused by an increased content of oxides in a sample. This is relevant to the sample N8 and agrees well with results of von Behren et al. [24]. Due to the oxidation effects which could prevail over pore growth processes if the concentration of HF in the acid mixture is relatively low, almost no changes in the morphology and only small variations in the crystallite size of the porous structures N8, N11

were observed while performing PL measurements at room temperature. More reliable results were obtained when performing PL measurements at liquid nitrogen temperature (77 K). These results were comparable with those obtained using experimental data of XRD analysis and Raman spectroscopy. Small differences in nanocrystallite size were possible, since Scherrer's formula does not account for the stress induced during the formation of porous structures.

Generally, increased porosity causes a PL peak shift to the higher energies. The decreased crystallite size in irradiated samples is closely related to the increased porosity of the porous structures due to pore growth. This statement agrees well with the increased intensity of the Raman spectra. According to Kompan et al. [25] and Kaabi et al. [1], it corresponds to the more intensive light penetration into the samples due to the decreased material density. However, according to our estimates (Table 2), exceptions are possible when two samples prepared in different conditions have the same porosity (samples N11 and N20). This may be related to the thickness of the N11 porous layer which is almost twice as thick as the samples from the same group.

4. Conclusions

Electrochemical etching is the most effective method for the production of regular porous silicon structures used in electronic devices of different application. However, this is not the best way to form porous silicon for solar cells or produce large area photodectors and other devices. The vapour etching method is relatively simple as compared with the electrochemical method. Using this technique, pyramid-like hillock porous silicon surface, essentially formed of interconnected cluster structures, is produced. It is easy to coat a thin, rough and homogeneous surface layer with an active metal and modify its reflectance and photoluminescence properties.

The surface morphology and porosity of silicon layers produced using chemical etching in the vapour-phase of an HF:HNO₃ acid mixture depends on the technological parameters of its fabrication. The present study has shown that vapour etching is responsible for the growth of differently sized and shaped pores randomly distributed in the fabricated inhomogeneous porous Si layers. Lower HF concentrations in the HF : HNO₃ mixture supported pore growth into the depth, and the prolonged

etching time, while keeping a constant relatively high HF concentration in the acid mixture, and responsible for the increased active surface of pores. The presence of crystalline, amorphous and porous Si in the produced porous layers was shown by the results of FTIR and Raman spectrometry. The presence of clusters of different size nanocrystallites was indicated in the skeleton of porous layers. Applying different methods based on experimental XRD, Raman and photoluminescence measurements, crystallite size was found to be 3.1–4.3 nm. It was related to the porosity of fabricated layers: the porosity of a layer was lower when the content of HNO₃ in the acid mixture was higher, indicating formation of mesoporous structures. An increasing porosity was observed upon increasing the etching time of samples when a relatively high concentration of HF in the HF : HNO₃ mixture was kept constant during the lengthy fabrication process. It has been shown that by varying the technological parameters and conditions of the vapour-phase etching process it is possible to control porosity and crystallite size in the fabricated porous silicon films and to produce Si nanostructures with an enhanced active surface layer.

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ĖSDINIMO GARŲ FAZĖJE ĮTAKA FORMUOJAMO PORĖTOJO SILICIO PAVIRŠIAUS MORFOLOGIJAI IR SANDARAI

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Santrauka

Analizuojama porėtojo silicio, suformuoto taikant cheminio ėsdinimo rūgščių HF : HNO₃ garų fazėje metodą, struktūra ir savybės. Keičiant ėsdinimo proceso parametrus buvo suformuoti įvairaus porėtumo sluoksniai, besiskiriantys porų forma ir dydžiu, taip pat aktyviau pavidavusiu plotu. Porėtojo Si sluoksnių sandara ir savybės tirtos Rentgeno difrakcijos, Ramano spektroskopijos, infraraudonųjų spindulių spektrometrijos ir fotoluminescencinės spektroskopijos metodais. Sluoksnių vaizdinimui, taip pat jų morfologijai tirti buvo naudojamas nu-

skaitantis elektroninis mikroskopas. Vertinant sluoksnių porėtumą, buvo panaudoti optinės elipsometrijos metu nustatyti eksperimentinių darinių lūžio rodikliai. Vertinant kristalitų dydį, buvo atsižvelgiama į porėtojo, kristalinio ir amorfinio silicio komponentus eksperimentiniuose dariniuose. Nustatyta, kad kristalitų dydis tirtuose porėtuose sluoksniuose kito nuo 3,1 iki 4,3 nm, o skirtingų bandinių porėtumas – nuo 61,4 iki 86,7 %.

Remiantis gautais rezultatais, aptariamas mezoporėtųjų darinių su nanokristalmais formavimas, kontroliuojant cheminio ėsdinimo garų fazėje parametrus.