

PECULIARITIES OF FORMATION AND OPTICAL PROPERTIES OF NANO-, MESO- AND MACROPOROUS SILICON

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Abstract. Some features of formation of porous silicon, its morphology and composition, as well as its optical properties were investigated in this work. Porous silicon was obtained on the substrates of single-crystalline Si as well as on the structures with p-n junctions. In order to obtain different structures of nano-, meso- and macroporous silicon as well as multi-layered porous structures several technological parameters were changed — orientation of substrates, conductivity type and composition of the etching solution. Correlation between photoluminescence intensity of the obtained samples and intensity of the absorption band in their IR spectra (the band at 616 cm^{-1}) that is due to the presence of Si-Si bonds in porous layer. The influence of porous silicon storage in the air on the degradation of photoluminescence parameters of porous silicon was estimated.

Keywords: porous silicon, Infrared spectroscopy, photoluminescence.

INTRODUCTION

At present a lot of investigations are performed in the area of design of various structures on the basis of porous silicon (por-Si) for a number of practical applications. Porous silicon obtained on highly-doped substrates of crystalline silicon is very prospective for a design of the optical waveguides, solar cells and avalanche LEDs [1, 2]. At the same time por-Si obtained on the substrate with the resistivity of 1—5 Ohm·cm can be used for producing of microactuators, self-destructed silicon chips, different silicon membranes for filters [3, 4]. If the wafers with the higher resistivity are used it is possible to produce microreactors, microresonators, photonic crystals, etc. [5—7]. One of the prospective abilities to use porous silicon is its application as sensitive elements in different sensors [8].

Porous silicon is not surely the best material for these applications. However, a possibility of integration of the optoelectronic devices based on por-Si with the elements and units of existing electronic circuits into a common module represents serious advantages as compared with the other approaches to the problem. Moreover, a controllable electrochemical etching, the choice of composition of the etching solution, further treatment of the samples in different gaseous environments or in organic/inorganic compounds, incorporation of metal ions and atoms into

the pores as well as deposition of masking layers make it possible to govern the functional characteristics of porous silicon for in order to optimize them for practical application [9, 10].

Optical parameters of porous materials are considerably determined by morphology of the pores and composition of the porous layers. Therefore the aim of the work was a determination of the dependence between optical characteristics of photoluminescence spectra and parameters of IR spectra for the different structures of nano-, meso- and macroporous silicon — IR spectra correlate with the chemical composition of investigated material. The role of porous layer oxidation in the change of photoluminescence spectra was determined when the samples were stored in the atmosphere for rather long time.

EXPERIMENTAL TECHNIQUE FOR OBTAINING OF THE SAMPLES AND MORPHOLOGY OF POR-Si

Surface composition of porous silicon, direction of pores growth, their sizes and morphology as well as porous layer thickness depend on the type and doping degree, crystalline orientation of original silicon wafer, composition and temperature of etching solution and on the etching mode. In the work porous silicon was obtained by electrochemical etching of single-crystalline silicon plates as well as silicon struc-

tures with p-n junctions in the alcoholic solutions of fluoric acid. Composition of HF alcoholic solutions and etching parameters varied insignificantly due to some specific features of electrochemical etching of silicon plates with p-n junctions. In one case we used an alternative etching solution based on dimethylformamide (DMFA) ((CH₃)₂NC(O)H) and HF in order to obtain porous silicon that did not show photoluminescence in the visible spectral range [9]. Parameters of

obtaining of the investigated samples and their basic characteristics are given in our previous works [9—13].

All of the samples of porous silicon were obtained actually in one day and after that they were stored in the air in laboratory conditions for 30 days. Technological parameters of the techniques used for obtaining the samples are presented in Table 1. The samples are enumerated according to the order of their obtaining in the laboratory unit.

Table 1. Modes of obtaining and characteristics of the investigated por-Si samples [9—13]

Sample designation	Original plate, resistivity ρ , Ohm·cm	Composition of the etchant	Current density and etching time	Pores sizes, according to SEM data, nm
3	KEF (100), 0.3	HF:C ₃ H ₇ OH: H ₂ O ₂	15 min, ~ 30 mA/cm ²	50—100
7	KEF (111), 1.0	HF:C ₃ H ₇ OH: H ₂ O ₂	15 min, ~ 30 mA/cm ²	50—100
18	KEF (100), 0.3	DMFA:HF: H ₂ O ₂	15 min, ~ 30 mA/cm ²	150—200
29	KEF (111), 10	HF:C ₃ H ₇ OH: H ₂ O ₂	15 min, ~ 50 mA/cm ²	Less than 10
30	Multi-layered KDB (11) p-/n structure p-layer: 0.4 n-layer: KEF (111), 10	HF:C ₃ H ₇ OH: H ₂ O ₂	25 min, ~ 30 mA/cm ²	a) p-layer ~ 1000—2000 б) n layer under p layer — pores of different diameter. Small pores are less than 30 nm, large ones — up to 2000 nm.

Scanning electron images of the cleavages were obtained with scanning electron microscope (SEM) produced by JEOL Co — JSM 6380LV (Figs. 1 and 2). Microscope images of porous silicon obtained on the substrates of KEF (doped by phosphorus) <100> (sample 3) and KEF <111> (sample 7) obtained in the alcoholic solution of fluoric acid, as well as porous silicon obtained on the substrates of KEF <100> (sam-

ple 18) in a solution of DMFA — fluoric acid in the same etching mode are presented in Fig. 1.

Analyzing the images one can note that the substrate orientation at the small difference in the doping level has a considerable effect on the morphology of pore formation, but only slightly influences on the diameter of large vertical pores. The difference in morphology is in appearance of smaller lateral pores

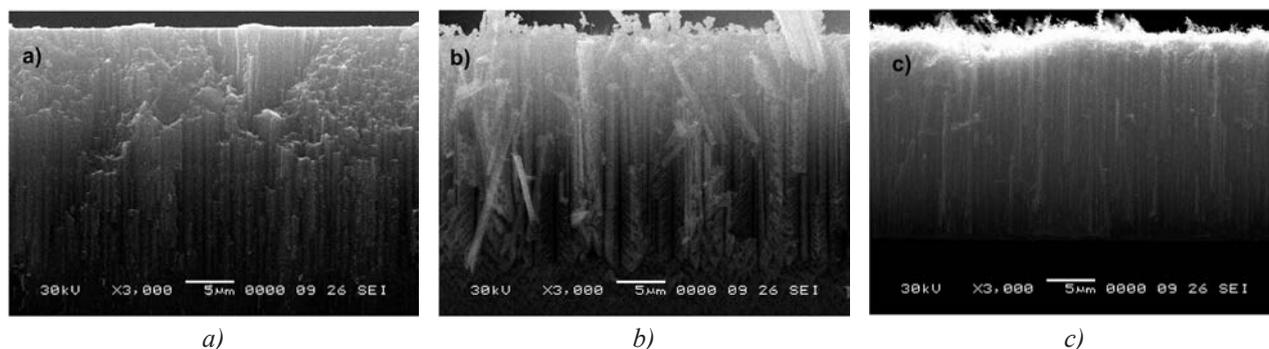


Fig. 1. SEM images of porous silicon cleavages: a) sample № 3, b) sample № 7, c) sample № 18

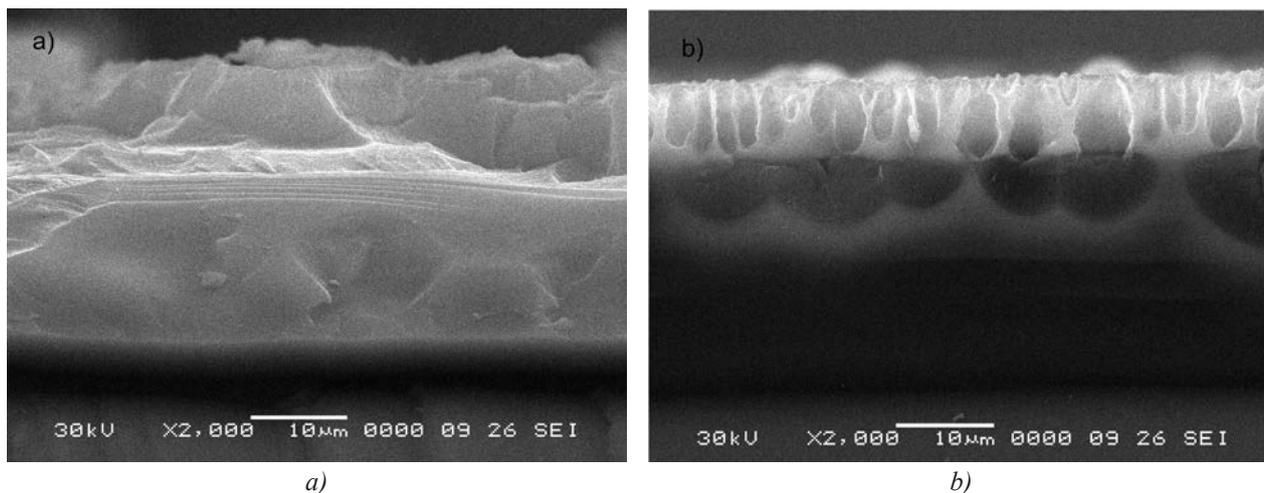


Fig. 2. SEM images of porous silicon cleavages: a) sample № 29, b) sample № 30

in the form of “herring-bone” in the porous silicon grown on $\langle 111 \rangle$ substrates. These features are due to the difference in the directions of the most optimal release of silicon ions in the process of electrochemical etching.

Porous silicon samples obtained with the use of DMFA-fluoric acid solution were characterized by a greater mean diameter of the vertical pores than in por-Si obtained by a standard technique with the use of alcoholic etchant at the same technological parameters. This could be due to the differences in the composition of the etchant solution providing another rate of the charge exchange between the electrolyte and silicon substrate [9, 14]. Thickness of the porous layer for the samples of 3, 7 and 18 was of $\sim 15 \mu\text{m}$.

Fig. 2 represents SEM images of porous silicon samples obtained by electrochemical etching of the plate KEF $\langle 111 \rangle$ with n-type conductivity and resistivity of $10 \text{ Ohm}\cdot\text{cm}$ (sample 29) and the plate KEF $\langle 111 \rangle$, $10 \text{ Ohm}\cdot\text{cm}$ with epitaxially grown p-layer of KDB $\langle 111 \rangle$ (doped by boron) with a resistivity of $0.4 \text{ Ohm}\cdot\text{cm}$ (sample 30). Technique for obtaining of such samples were previously described in our work [12].

Porous layer thickness in the sample 29 was of $\sim 30 \mu\text{m}$, and in this sample no any pores with the diameter more than 10 nm were observed. At the same time this sample demonstrated rather good photoluminescence properties that in combination with the standard technique for producing of porous silicon in the etchant on the basis of alcoholic etching solution made it possible to consider it as a nanoporous silicon. Comparison of morphology of the sample 29 with the samples 3 and 7 demonstrated that under etching in the same technological modes pore diameter for the highly

doped samples is greater than for low-doped ones. This can be easily explained by the presence of much more amount of the impurity defects facilitating formation of the pores with the sizes of $10\text{--}100 \text{ nm}$.

In SEM images of the cleavage for the sample 30 formed at p/n junction from the side of p-layer two clearly expressed porous layers can be observed with the different sizes of the ordered vertical macropores as well as the interface between these two layers. Thickness of the layers was of $\sim 10 \mu\text{m}$ for p-layer and $\sim 15 \mu\text{m}$ for the underlying layer of n-por-Si. Next some part of p-layer was mechanically removed and after that IR and photoluminescence (PL) investigations were performed as for the top layer (designated as sample 30-p), as for the underlying layer (designated as 30-n).

PHOTOLUMINESCENCE AND IR SPECTROSCOPY OF POROUS SILICON

The origin of visible photoluminescence (PL) in porous silicon yet remains a subject of scientific controversy. At present there are several hypotheses on the mechanisms and models of photoluminescence in porous silicon: quantum-size model [15, 16], model of luminescence as a result of formation Si-H bonds appearing in the process of formation amorphous-like layer on the surface of (nano) wires in por-Si [17—19] and some others. To elucidate the role of surface defects, and also the substances adsorbed on the surface of the crystallites in porous layer as well as to understand the effect of technology of porous silicon obtaining we studied photoluminescence spectra of this material obtained by different methods, as soon after obtaining the samples as after their storage in the atmosphere for a certain time.

Measurements of PL spectra were performed with the automated spectral-luminescent unit based on monochromator MDR-4. Semiconductor laser with the wavelength of 405 nm corresponding the energy of 3.05 eV was applied for the excitation photoluminescence.

Photoluminescence spectra for the samples of porous silicon, excited with the laser at the wavelength

of 405 nm are presented in Fig. 3. It should be noted that under PL excitation with the source having wavelength of 532 nm just the same ratio of intensities for the investigated samples was observed as in the case of 405 nm laser (see Table 2), except the fact that the integral PL intensity was lower.

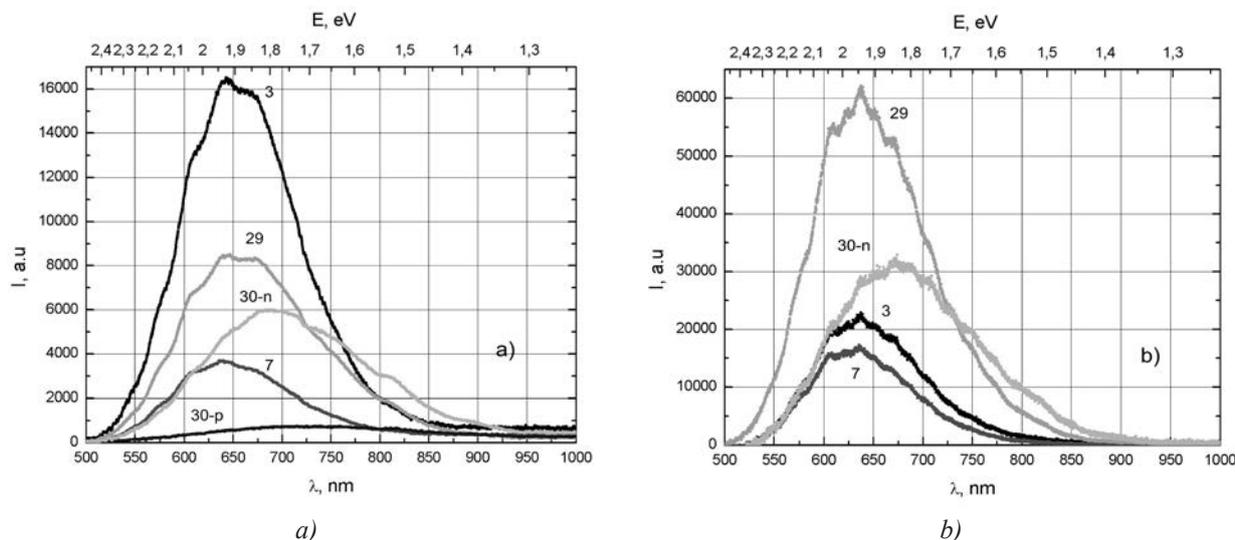


Fig. 3. PL spectra of porous silicon samples under excitation with the light source — laser with the wavelength of 405 nm: a) storage for 30 days; b) storage for 120 days

Table 2. Intensity and position of the main PL peak for the samples of porous silicon

Sample	PL intensity for 405 nm source, a. u.	PL intensity for 532 nm source, a. u.	Position of PL peak, 405 nm source, eV	Position of PL peak, 532 nm source, eV
3	16000	11500	1.93	1.78
30 — n layer under p-layer	6000	5000	1.80	1.65
29	8000	4500	1.93	1.78
7	3600	600	1.93	1.86
30 p-layer	600	300	1.7	1.6

Analysis of the data on PL shows that the most intensive photoluminescence demonstrated the sample № 3, and a little less intensive spectra are characteristic of the samples 29 and 30-n. Position of the main luminescence peak for all of the samples is within the range of ~ 1.8—1.9 eV, while under PL excitation with the laser operating at 532 nm the peak is shifted by 0.05—0.15 eV towards less energy range as compared with the PL spectra obtained with 405 nm laser. The shape of PL band under excitation with different sources changed insignificantly.

Main parameters of PL spectra for the investigated porous silicon samples are presented in Tab 2.

For elucidating of the influence of the surface composition on the photoluminescence of porous silicon we performed the investigations of the samples by IR spectroscopy technique. IR transmission spectra of porous silicon samples were obtained IR Fourier spectrometer Vertex 70 (Bruker) with the use of attachment for the attenuated total internal reflection (FTIR ATR) (Fig. 4).

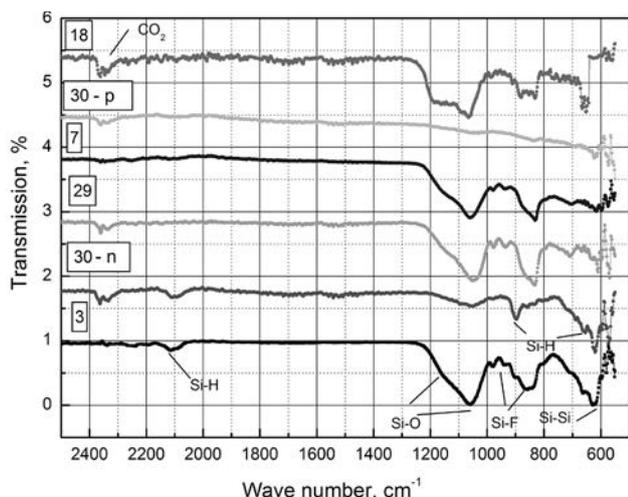


Fig. 4. Transmission IR spectra of porous silicon samples with the different pore sizes after 30 days of storage

The estimate calculations show that the depth of analysis for this technique for the samples of porous silicon for the wave numbers up to 2000 cm^{-1} does not exceed $1.5\text{ }\mu\text{m}$, while for the range of $2000\text{—}4000\text{ cm}^{-1}$ — it does not exceed $10\text{ }\mu\text{m}$. Thus one obtains the data on the chemical bonds just within the thickness of porous layer.

Analyzing IR transmission spectra of porous silicon samples one can see the presence of several specific features that are characteristic for this material [19], corresponding to the vibrations of Si–Si (616 cm^{-1}), Si–H ($664, 804, 906, 2100\text{—}2140\text{ cm}^{-1}$), Si–O ($1060\text{—}1170\text{ cm}^{-1}$). Moreover, in the spectra of the samples there are absorption bands corresponding to the adsorbed CO_2 (2360 cm^{-1}) and the traces of surface contamination with the etchant solution, probably due to the formation of Si–F bonds (830 and 950 cm^{-1}).

Comparing data, obtained by IR spectroscopy with PL characteristics of por-Si samples one can note the following regularities: first, in IR spectra of all the samples with rather bright photoluminescence within the visible range an expressed quite broad band at $600\text{—}700\text{ cm}^{-1}$ is observed with a peak approximately near 616 cm^{-1} , that is characteristic for Si–Si bonds. For the samples with less PL intensity this band is also less expressed and it completely disappears for the samples that do not demonstrated PL properties in the visible range. This peculiarity can be explained by the presence of a great amount of silicon nanocrystals/nanoclusters in the samples with a bright photoluminescence that is in a good agreement with the results our previous investigations [10, 11]. This effect can get rather important practical application as a method

of express-test of the obtained porous silicon suitable for optoelectronics requirements by IR spectra (FTIR ATR). However, this peculiarity can not be revealed in case of the deposition of different coatings on the surface of porous silicon including metal films, different masks and so on due to the appearance of additional radiative and non-radiative recombination levels in the obtained structure resulting in the changes in PL mechanisms.

Second distinctive feature of IR spectra of por-Si samples demonstrating a bright photoluminescence is the presence of absorption band due to S–H bonds in the range of $2100\text{—}2140\text{ cm}^{-1}$. Taking into account that these bonds are rather weak, they can actively participate in the different natural or technological processes on the sample surface, such as oxidation, carbonization, etc., resulting in enhancement or more often in a decrease of the luminescence properties of por-Si. This phenomenon also proposes the possibilities for development of the control for the functional characteristics of the porous silicon structures for optoelectronic devices and various sensors.

Freshly obtained porous silicon is known to be gradually oxidized in the air; the most rapid oxidation processes take place during the first days after por-Si growth [11, 20]. Then a slow oxidation continues while storing of porous silicon in the atmosphere [11, 20]. The later process is not investigated in details as the rapid one.

Therefore, in connection with the observed correlations between IR spectra and photoluminescence of the investigated samples with the pore sizes from several nanometers to several μm it seems actually interesting to investigate the behavior of the optical characteristics of por-Si with rather long period of time. So after 3 months of storage in the air the investigations of the obtained samples were repeated.

Morphology of the samples almost did not change. According to IR spectroscopy data a decrease of intensity of the absorption band can be observed in the range of $600\text{—}700\text{ cm}^{-1}$ and a noticeable increase of the band at $1000\text{—}1200\text{ cm}^{-1}$, corresponding to Si–O bonds, the rest absorption bands changed insignificantly. The samples which demonstrated very weak photoluminescence or even its complete absence actually did not show any considerable changes of their IR spectra.

To show the results more clearly we can separately compare PL and IR spectra of “leaders”, kept in the atmosphere for 30 and 120 days. One can note that after 120 days of storage in the air the most bright PL is observed for the sample, which is characterized by the less changes in the shape and intensity of IR trans-

mission band within the range of $600\text{--}700\text{ cm}^{-1}$, meaning a preservation of the correlation between IR spectral shape of this band and PL properties of the samples with time.

To show the results more clearly we can separately compare PL and IR spectra of “leaders” (Designation “leader” means a group of samples with the highest PL intensity), kept in the atmosphere for 30 and 120 days (Fig. 5). One can note that after 120 days of storage in the air the most bright PL is observed for the sample, which is characterized by the less changes in the shape and intensity of IR transmission band within the range of $600\text{--}700\text{ cm}^{-1}$, meaning a preservation of the correlation between IR spectral shape of this band and PL properties of the samples with time.

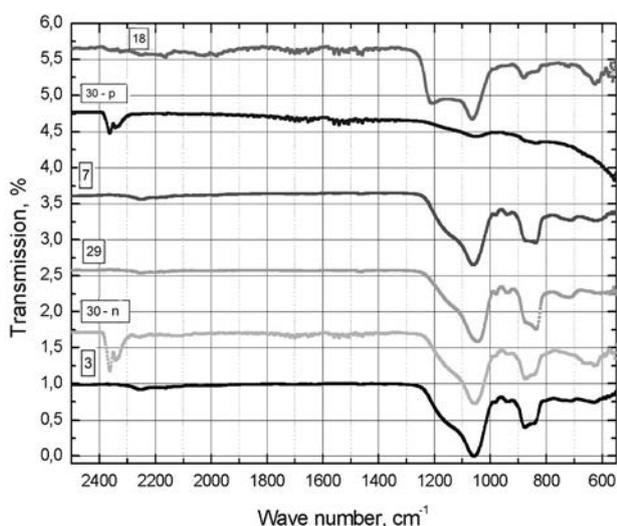


Fig. 5. Transmission IR spectra of porous silicon samples with different pore sizes after 120 days of storage in the air

In this work we do not consider and discuss the problems of the changes in absolute PL intensity for certain samples with time due to specific features of the experimental technique while measuring photoluminescence of the samples. However, in [11] we performed similar investigations for the samples like № 7 that demonstrated a decrease of photoluminescence of porous silicon with time due to the oxidation of their surface. Our results are in an agreement with the works of other researchers and our data on IR spectroscopy.

Note, that the relative PL intensity in the series of porous silicon samples changed after storage in the air. In this case the highest relative intensity was observed for the sample № 29, then followed the sample № 30-n; the former “leader”, sample № 3 shifted down to the third place by intensity. But neither main peak of PL, nor PL band did not actually shifted by the wavelength,

and the noticeable broadening of the band is also absent. In the same work [11], just as in lot of the others the shift of the luminescence band was observed to the less wavelengths with rather short periods of time when the samples were stored in the atmosphere (for several days). This shift is usually explained by the oxidation of silicon nanoclusters at the surface of porous layer.

The absence of such shift in the case of the samples studied in this work can be interpreted as follows. Unlike of the results showing PL shift in porous silicon to the shorter wavelengths at the oxidation both of our experiments were performed for rather long time after producing the samples — 30 and 120 days, respectively. It seems reasonable to assume that in this case the processes of natural ageing including oxidation and reconstruction of Si-Si bonds at the surface of pores and inside Si wires proceed very slowly as compared with the initial stage of the storage. In our opinion a decrease of silicon clusters in the surface layers is rather slow due to progressive formation of more compact oxide shell surrounding Si clusters. Surely, very small clusters can be completely oxidized during long periods of storage, but this is compensated by the oxidation of the deeper layers and formation of the clusters surrounded by oxide shell deep inside the porous layer. A decrease of PL intensity can be connected as with the change in the number of defects in the surface layers due to appearance of mechanical stresses after oxidation as with the total reduce of the number of silicon nanocrystals just on the surface due to their complete oxidation.

CONCLUSION

As a result of the investigations made in the work it was found that for all of the samples having the brightest photoluminescence within the visible optical range a wide band in the IR spectra is clearly observed at $600\text{--}700\text{ cm}^{-1}$ with the main peak at 616 cm^{-1} , characteristic of Si-Si bonds.

For the samples with less intensive PL this band is expressed in a less extent and it completely disappears for the samples that do not demonstrate any PL properties. This peculiarity can be explained by the presence of a considerable amount of silicon nanocrystals/nanoclusters in the porous layer that is in a good agreement with the previous investigations. Under storage in the air for a long time PL intensity for different samples was reduced in different manner but this decrease at least qualitatively correlated with a decay of intensity of the absorption band in IR spectra at the range of $600\text{--}700\text{ cm}^{-1}$; at the same time the absorption band at $\sim 1020\text{ cm}^{-1}$ corresponding to Si-O bonds was clearly enhanced. It means that the correlation noted above

was kept. The shape and intensity of the other absorption bands of the IR spectra was changed to a less extent.

A decrease in sizes of silicon nanoclusters in the surface layers in the process of a long-term natural oxidation during por-Si storage in the atmosphere seemed to result in a shift of PL band to the shorter wavelengths. However, it was not observed in our experiments. In our opinion, the processes of decrease of nanosilicon cluster sizes for the samples exposed in the atmosphere, proceed more slowly due to a gradual formation of more compact oxide shell around silicon core. Besides, an oxidation of the deeper por-Si layers occurs under longer time of the sample storage in the atmosphere.

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REFERENCES

1. Bondarenko V. P., Yakovtseva V. A., Dolgij L. N. // Pis'ma v Zhurn. Tekhnich. Fiziki. 1999. V. 25. Iss. 17. P. 69—73.
2. Lazaruk S. K., Leshok A. A., Labunov V. A. // Fizika i Tekhnika Polupr. 2005. V. 39. Iss. 1. P. 149—152.
3. Lazaruk S. K., Dolbik A. V., Labunov V. A. // Fizika i Tekhnika Polupr. 2007. V. 41. Iss. 9. P. 1130—1134.
4. Goryachev D. N., Belyakov D. N., Sreseli O. M. // Fizika i Tekhnika Polupr. 2010. V. 44. Iss. 12. P. 1636—1639.
5. Aktsipetrov O. A., Dolgova T. V., Soboleva I. V. // Fizika Tverdogo Tela. 2005. V. 47. Iss. 1. P. 150—152.
6. Astrova E. V., Borovinskaya T. N., Perova T. S. // Fizika i Tekhnika Polupr. 2004. V. 38. Iss. 9. P. 1121—1124.
7. Zharova Yu. A., Fedulova G. V., Astrova E. V. // Fizika i Tekhnika Polupr. 2011. V. 45. Iss. 8. P. 1136—1143.
8. Moshnikov V. A., Gracheva I. E., Lenshin A. S. // J. of Non-Crystalline Solids. 2012. V. 358. Iss. 3. P. 590—595.
9. Kashkarov V. M., Lenshin A. S., Seredin P. V. // Poverkhnost'. Rentgenovskie, Sinchrotronnye i Neitronnye Issledovaniya. 2012. № 9. P. 80—86.
10. Lenshin A. S., Kashkarov V. M., Tsipenyuk V. N., Seredin P. V. // Zhurn. Tekhnich. Fiziki. 2013. V. 83. Iss. 2. P. 36—140.
11. Lenshin A. S., Kashkarov V. M., Turishchev S. Yu., Smirnov M. S., Domashevskaya E. P. // Pis'ma v Zhurn. Tekhn. Fiziki. 2011. V. 37. Iss. 17. P. 1—8.
12. Lenshin A. S., Kashkarov V. M., Seredin P. V. // Fizika i Tekhnika Polupr. 2012. V. 46. Iss. 8. P. 1101—1107.
13. Lenshin A. S., Kashkarov V. M., Minakov D. A. // Zhurn. Tekhnich. Fiziki. 2013. V. 83. Iss. 3. P. 96—100.
14. Kashkarov V. M., Lenshin A. S., Seredin P. V., Minakov D. A. // Izvestiya Vuzov. Materiali Elektronnoi Tekhniki. 2013. № 2. P. 55—59.
15. Canham L. T. // Appl. Phys. Lett. 1990. V. 57. № 10. P. 1046—1048.
16. Korsunskaya N. E., et al. // Fizika i Tekhnika Polupr. 2010. V. 44. Iss. 1. P. 82—86.
17. Salonen J., et al. // Appl. Surf. Sci. 1997. V. 120. P. 191—198.
18. Lenshin A. S., Kashkarov V. M., Seredin P. V. // Fizika i Tekhnika Polupr. 2011. V. 45. Iss. 9. P. 1229—1234.
19. Domashevskaya E. P., Terekhov V. A., Kashkarov V. M., et al. // Khimia Poverkhnosti i Sintez Nizkorazmernykh Sistem: Sbornik nauchn. trudov. SPb., 2002. P. 29—40.
20. Lenshin A. S. Features of formation of porous silicon and its nanocomposites. Saarbrücken: Lap Lambert Academic Publishing, 2013. 218 p.

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