

CHANGE IN THE PHOTOLUMINESCENCE PROPERTIES OF STAIN ETCHED POROUS SILICON AFTER POSTTREATMENT IN VARIOUS ACID AND ALKALINE ETCHANTS

F.A. RUSTAMOV, N.H. DARVISHOV, V.E. BAGIEV, M.Z. MAMEDOV,
E.Y. BOBROVA, H.O. ASKEROVA

*Condensed Matter Physics Division, Institute for Physical Problems,
Baku State University, Baku AZ 1148, Azerbaijan*

E-mail: farhad.rustamov@bsu.edu.az

The effect of posttreatment in aqueous solutions of HF, KOH, NaOH and Na₂SeO₃ on the photoluminescence spectra of stain etched porous silicon has been investigated. It is shown that this posttreatment of as-prepared samples leads to a shift of the photoluminescence maximum from ~1.85 eV to 2.1 eV. Subsequent atmospheric oxidation during 2÷3 min leads to the transformation of the spectra, and its maximum shifts back to 1.85 eV. The intensity of photoluminescence after posttreatment of porous silicon depends on the composition of the etchant. In the HF solution, the photoluminescence intensity hardly changes, while in alkaline solutions it decreases. This is due to the different etching rates of silicon and silicon oxide in different etchants. The role of oxygen bonds in the formation of local radiative recombination levels in the band-gap, responsible for photoluminescence transformations, is discussed.

Keywords: porous silicon; stain etching; posttreatment; diluted HF; alkaline solutions; yellow PL; oxygen bonds
PACS: 81.40.-z; 78.67. Rb; 78.55.-m

1. INTRODUCTION

The phenomenon of visible photoluminescence (PL) in porous silicon (PS) has been intensively studied from both a practical and theoretical point of view since its discovery [1, 2]. From a practical point of view, this material has potential possibilities of practical application in micro- and optoelectronics, photovoltaics, biomedicine, as chemical and biological sensors, antireflection coating for solar cells, and so on [3, 4]. From a theoretical point of view, it is of interest to find out the physical mechanism of this phenomenon [5, 6]. Being an indirect-gap semiconductor with a band gap of 1.1 eV and with a lot of dangling bonds on the surface, a bulk crystal doesn't exhibit visible PL. After electrochemical or purely chemical etching, the transformed material, called porous silicon, begins to exhibit visible luminescence with a maximum higher than 1.1 eV. At present, it has been established that this is primarily due to the quantum size effect broadening the band gap in silicon nanocrystallites, which are obtained during the technological process of PS formation. And indeed, especially at small porosities, it is observed that with an increase in porosity, i.e. with a decrease in the size of silicon nanocrystallites, a shift of the maximum PL to the high - energy region is observed [3, 4, 7]. But only the quantum-size effect cannot explain all observed experimental facts. In particular, at high porosities, the further shift of the PL maximum to the high - energy region stops [3, 4]. This experimental fact can be explained by the appearance, due to surface states, of radiative recombination levels located in the band gap. Theoretical works indicate that these levels arise during the oxidation of silicon crystallites [5, 6]. It is shown, that when hydrogen bonds Si-H are replaced by oxygen bonds Si-O, local levels appear in the band gap of PS. Moreover, depending on the formation method of PS, this substitution can occur both during PS formation [8-11]

and during atmospheric oxidation after formation [12-14]. It is the appearance of such radiative recombination levels that leads to red - orange photoluminescence, regardless of the porosity and size of silicon nanocrystals.

The PS samples, obtained by stain etching, are usually highly porous, and oxygen bonds in them are formed in the process of the formation of porous silicon in the etching solution [11]. As a consequence, instead of band-to-band transitions, transitions through these local levels prevail here. As a result, stain-etched porous silicon, regardless of porosity, exhibits stable red-orange or orange PL immediately after preparation. To shift the PL maximum in these PS samples, it is necessary to remove these oxygen bonds.

As is known, the silicon surface is well etched with aqueous solutions of HF and alkalis. But the effects of these solutions are different from each other. Depending on the type of etchant, its concentration, and etching duration, postetching can lead to the removal of oxygen bonds, a further reduction in the size of Si nanocrystallites, as well as to etching of the silicon itself, and a decrease in the thickness of the PS layer. Therefore, the final result of the effect of posttreatment on the maximum and intensity of PL requires further experimental research and comparative analysis.

In this work, we studied the effect of posttreatment on the PL spectra of stain etched porous silicon in HF, KOH, NaOH and Na₂SeO₃ solutions of various concentrations.

2. EXPERIMENT

Porous silicon samples were obtained by stain etching on p-type monocrystalline silicon substrates with a resistivity of 0.1 Ohm·cm and (111) orientation. To remove contaminant and degrease the surface, the plates were immersed in acetone for 50 min and then washed with bidistilled water. Then, to remove the

oxide layer, the surface of the plates was treated in a 10% aqueous HF solution for 1 min and then in concentrated HF (50%) for 5 min [19]. PS layers were formed at room temperature under daylight illumination in an HF(50%):HNO₃(65%):CH₃COOH (glacial) modified solution in a volume proportion of 1200:1:800, i.e., at oxidant insufficiency [20]. After the incubation time, the reaction of PS formation lasted 9 min. Such samples have a porosity of more than 70%, with crystallite sizes of 1.5–2.8 nm [9, 21, 22]. Some of the samples immediately after the formation of PS were washed in bidistilled water and then was treated in various acid and alkaline etchants. It was very important to prevent contact of the PS with atmospheric air when transferring the obtained sample from the cleaning solution to the etching solution. PS samples were postetched in the following etchants: 10% aqueous solution of HF, NaOH, KOH and Na₂SeO₃ aqueous solutions in 0.0001M, 0.001M, 0.01M and 1M concentration within 1÷60 minutes. Then the samples were washed in bidistilled water, isopropyl alcohol and

dried by N₂ jet. Immediately after drying, the PL spectra of the obtained samples were studied under ambient atmospheric conditions.

The PL spectra have been investigated at room temperature. The PL was excited by a Xenon lamp DKSL-1000, passed through an SPM-2 monochromator, and was recorded with an IKS-12 monochromator in the reflection geometry. In PL measurements, the excitation wavelength was 320 nm.

3. RESULTS

Fig.1 shows the PL spectra of stain etched PS samples both immediately after formation (a) and after posttreatment (b) in an alcohol solution of 10% HF in a volume proportion of 1:1. An alcohol solution was used to increase wettability. As can be seen from the figure, the samples that have not undergone additional treatment exhibit red PL with a peak at ~1.85 eV (Fig.1a).

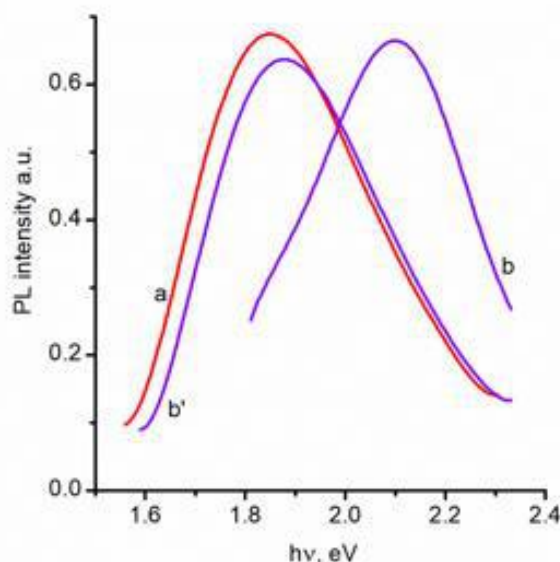


Fig.1. PL spectra of stain etched PS without and with posttreatment in dilute HF. a) as-prepared PS without postetching; b) as-prepared PS immediately after postetching in dilute HF; b') postetched PS after 5 min exposure in air.

This is a common PL spectrum observed in relatively highly porous PS samples obtained by conventional electrochemical or stain etching methods without posttreatment. Those samples that were subjected to posttreatment in an alcohol solution of 10% HF for ~ 10 min immediately after formation exhibit yellow PL with a maximum at 2.1 eV (Fig.1b). I.e. such additional etching of PS samples leads to a shift of PL peak to high-energy region (Fig.1, transition a → b). Upon contact with air, this PL spectrum is transformed very quickly (1 ÷ 3 min) and its maximum shifts back to ~ 1.85 eV (Fig.1, transition b→b'). As can be seen from Fig.1 the PL spectra of untreated samples and samples posttreated in an alcohol solution of 10% HF and exposed in air for more than 5 min practically coincide. Further exposure in air leads to a slight

increase in the PL intensity without shifting its maximum.

Fig. 2 depicts the characteristic PL spectra of PS samples after 2 minutes of posttreatment in aqueous solutions of KOH of various concentrations. The PL spectra of PS samples subjected to posttreatment in aqueous solutions of NaOH and Na₂SeO₃ are not given because of their similarity to the spectra in Fig.2. As can be seen from the PL spectra, the posttreatment of PS samples in alkaline etchants also leads to a shift of the PL maximum to the high-energy region (Fig.2, transition a → b), i.e., red PL (~1.85 eV) turns into yellow (~2.1 eV). However, as shown in Fig. 2b, there is a significant decrease in intensity compared to the previous case's additional treatment in diluted HF in Fig. 1b.

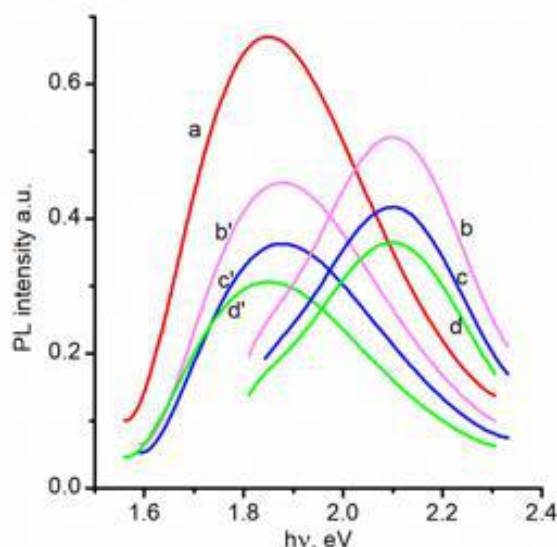


Fig.2. PL spectra of stain etched PS without and with posttreatment in KOH solutions. a) as-prepared PS without postetching; b) and b') PS postetched in 0.001M KOH immediately and after 5 min exposure in air; c) and c') PS postetched in 0.01M KOH immediately and after 5 min exposure in air; d) and d') PS postetched in 1M KOH immediately and after 5 min exposure in air.

Further exposure to air, as in the previous case, leads to the reverse shift of the PL peak to the initial position of 1.85 eV, but with a significant decrease in the intensity (Fig.2, transition b \rightarrow b'). The increase in the concentration of etching alkaline solution doesn't change the position of the corresponding maxima, and it only leads to a decrease in intensity at each stage (Fig.2, transitions c \rightarrow c' and d \rightarrow d').

4. DISCUSSION

The PL emission spectra shown in Fig.1a and Fig.2a correspond to stain etched PS without posttreatment. These are typical PL spectra of PS, with a maximum in the red - orange region. Such spectra are observed both in the electrochemical and stain etching methods of PS formation. The reason for such PL is a total manifestation of the quantum-size effect in silicon nanocrystallites and their surface oxidation. The quantum-size effect expands the band-gap and surface oxidation leads to the appearance of local levels of radiative recombination. In the case of low PS porosity when the sizes of silicon nanocrystals are larger than ~ 4 nm, these local levels are located inside the conduction band and do not show up in the PL emission spectrum [5, 6]. In this case, PL is a consequence of radiative zone-to-zone transitions. As the size of nanocrystals decreases, the peak of the PL spectrum slightly shifts to the high-energy region. But when the PS porosity is high and the size of nanocrystals becomes smaller than ~ 4 nm, the local level associated with surface states is located inside the band-gap. And, because radiative recombination occurs at these local levels in this case, a further decrease in the size of silicon crystallites, resulting in an increase in the width of the band gap, does not cause a shift in the PL maximum [5, 9, 22]. Such spectra are observed both in the electrochemical and stain etching methods of PS

formation. The difference in the PL spectra obtained by different methods manifests itself when they are oxidized in air immediately after their preparation. The PL spectra of PS samples in the first case are strongly transformed, while in the second case they are quite stable. Early Fourier spectral studies show that this is due to the oxygen bonds (Si-O-Si asymmetric stretching of interstitial oxygen in Si at the band of 1108 cm^{-1} and O3-SiH bending and stretching mode at 882 cm^{-1} and 2245 cm^{-1} absorption peaks) that are already formed during the PS formation process during stain etching [11, 13, 23,]. I.e. in these samples' local radiative recombination levels, located in the band-gap and associated with Si-O bonds, appear in the etchant solution as PS is formed. As a result, despite the size and porosity of silicon nanocrystallites (1.8-2.3 nm), as-prepared stain-etched PS exhibit only red-orange PL [21, 22].

A comparison of Fig.1 and Fig.2 shows that, upon postetching of PS in various solutions of HF and KOH, a similar transformation of the PL spectra occurs. In all cases, the posttreatment leads to a significant shift of the PL maximum from 1.85 eV to 2.1 eV (a \rightarrow b, a \rightarrow c, a \rightarrow d transitions). However, it should be kept in mind that such a shift can be detected only immediately after PS postetching, namely, only in as-prepared samples, until atmospheric oxidation affects. This similarity indicates the identity of the influence of various etchants on the PL mechanism. It is known that both dilute aqueous solutions of HF and alkaline aqueous solutions very quickly remove the oxide layer from the silicon surface [2, 5, 15 - 18]. Such a posttreatment of the samples in the above-mentioned etchants leads to the removal of Si-O bonds and, hence, to the removal of the local radiative levels located in the band-gap of silicon nanocrystallites. In the absence of these local levels in the band-gap, recombination occurs through band-to-band transitions, which is manifested in the

shift of the PL maximum from 1.85 eV to 2.1 eV. It should be noted that the position of the maximum of the PL spectrum (~2.1 eV) after postetching does not depend on the applied etchant, its concentration and the duration of postetching. Those, the limiting value of the maximum of the PL spectrum is always ~2.1 eV. Rather, this is the limiting value of the maximum PL which can be achieved in PC formed by electrochemical or stain etching methods [2, 13, 23, 24].

When exposed to atmospheric air, another similar transformation of the PL occurs (b→b', c→c', d→d' transitions). Within a few minutes, the PL peak reverse shifts from the yellow region (2.1 eV) to the low-energy red region (1.85 eV). This indicates the fact that silicon nanocrystallites are re-oxidized, which means that radiative recombination levels are again formed in the band-gap, leading to the observed shift of the PL peak. Radiative recombination proceeds again through these centers, regardless of the prehistory of sample processing.

The comparison of Fig.1 and Fig.2, in addition to the similarity in the shift of the PL maximum, also shows their difference in intensity behavior. The same reversible shift of the PL maximum red-yellow-red is observed after postetching PS in dilute HF solution or in alkaline KOH solutions followed by atmospheric oxidation. However, while after additional etching in HF solutions, the PL intensity remains almost unchanged, after additional etching in KOH solutions, the intensity noticeably decreases. Here, a different etching rate of silicon and its oxide in these etchants is manifested [2]. The posttreatment in a dilute HF solution for short etching times leads only to the removal of the oxide layer without changing the average size of Si nanocrystallites. In this case, the thickness of the luminescent layer almost does not change, and therefore the luminescence intensity also remains almost unchanged. In alkaline solutions, the etching rate of silicon and its oxide is high and grows with increasing concentration. As a result, when the PS is postetched in alkaline solutions, the thickness of the

luminescent layer decreases, resulting in a reduction in PL intensity. Since the rate of PS etching increases with an increase in the concentration of KOH, the thickness of the luminescent layer also decreases. Therefore, with an increase in the KOH concentration, the intensity of PL also decreases.

5. CONCLUSIONS

A comparative study of the effect of additional etching in various etchants on the photoluminescence of stain etched porous silicon was carried out. The PS layers were obtained on the Si wafers by stain etching in a HF:HNO₃:CH₃COOH solution at oxidant insufficiency. Immediately after formation all PS samples exhibited red PL (~1.85 eV). All samples were subjected to posttreatment in a dilute HF solution and various alkaline solutions. It was revealed that such posttreatment of the investigated samples always leads to a shift in the maximum of their PL maximum from the red (1.85 eV) to the yellow (~2.1 eV). This shift is associated with the removal of oxide layers from the surface of Si nanocrystallites and leads to the removal of radiative recombination levels in the band-gap. The removal of these levels leads to the predominance of band-to-band transitions in the PL spectrum. When exposed to air, the PL spectra transformed within 2-3 minutes due to atmospheric oxidation, and the PL maximum shifted back to the red region (2.1 eV 1.85 eV). This proves the decisive role of oxygen bonds on the PS surface in the PL mechanism. Despite the similarity in the PL maximum behavior, the posttreatment with various etchants affects its intensity in a different way. After additional etching in a dilute HF solution, the PL intensity remains almost unchanged. The postetching in alkaline solutions leads to a decrease in the PL intensity, and the higher the concentration of the solution, the lower the PL intensity. Such a change in the PL intensity is related to the different etching rates of silicon itself in these etchants.

-
- [1] *L.T. Chanham*. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafer, *Appl. Phys. Lett.* 57 (1990) 1046-1048. <https://doi.org/10.1063/1.103561>
- [2] *V. Lehmann, U. Gosele*. Porous silicon formation: A quantum wire effect, *Appl. Phys. Lett.* 58 (1991) 856-858. <https://doi.org/10.1063/1.104512>
- [3] *V. Lehmann*. *Electrochemistry of Silicon*, Wiley VCH, New York, 2002.
- [4] *L.T. Chanham*. Properties of porous silicon. EMIS Data Review Series No. 18, London, 1997.
- [5] *C. Delerue, G. Allan, M. Lannoo*. Theoretical aspects of the luminescence of porous silicon, *Phys. Rev. B* 48, 15 (1993) 11024-11036. <https://doi.org/10.1103/PhysRevB.48.11024>
- [6] *M.V. Wolkin, J. Jorne, P.M. Fauchet, G. Allan, C. Delerue*. Electronic States and Luminescence in Porous Silicon Quantum Dots: *Phys. Rev. Lett.* 82, 1 (1999) 197-200. <https://doi.org/10.1103/PhysRevLett.82.197>
- [7] *F.A. Rustamov, N.H. Darvishov, M.Z. Mamedov, E.Y. Bobrova, H.O. Qafarova*. Porous silicon bandgap broadening at natural oxidation. *J. Lumin.* 131, 10 (2011) 2078-2082. <https://doi.org/10.1016/j.jlumin.2011.05.040>
- [8] *Y.Q. Jia, L.Z. Zhang, J.S. Fu, B.R. Zhang, J.C. Mao*. Characterization of stain etched porous Si with photoluminescence, electron paramagnetic resonance, and infrared absorption spectroscopy, *J. Appl. Phys.* 74 (12) (1993) 7615-7617. <https://doi.org/10.1063/1.354940>
- [9] *É. Vázsónyi, E. Szilágyi, P. Petrik, Z. Horvath, T. Lohner, M. Fried, G. Jalsovszky*. Porous silicon formation by stain etching, *Thin Solid Films*. 388 (2001) 295-302. [https://doi.org/10.1016/S0040-6090\(00\)01816-2](https://doi.org/10.1016/S0040-6090(00)01816-2)
- [10] *B. González-Díaz, R. Guerrero-Lemus*,

- J. Méndez-Ramos, B. Díaz-Herrera, V.D. Rodríguez.* Gradual oxidation of stain etched porous silicon nanostructures applied to silicon-based solar cells. *Sens. Actuators, A* 150 (2009) 97–101 <https://doi.org/10.1016/j.sna.2008.12.006>
- [11] *F.A. Rustamov, N.H. Darvishov, V.E. Bagiev, M.Z. Mamedov, G.M. Eyvazova, E.Y. Bobrova, H.O. Qafarova.* Reversible quenching of photoluminescence in stain etched porous silicon at HNO₃ posttreatment and role of oxygen bonds. *J.Lumin.* 195 (2018) 49-53. <https://doi.org/10.1016/j.jlumin.2017.11.011>
- [12] *E. Kayahan,* The role of surface oxidation on luminescence degradation of porous silicon, *Appl. Surf. Sci.* 257(9) (2011) 4311-4316. <https://doi.org/10.1016/j.apsusc.2010.12.045>
- [13] *N. Arad-Vosk, A. Sa'ar.* Radiative and nonradiative relaxation phenomena in hydrogen- and oxygen-terminated porous silicon, *Nanoscale Research Letters.* 9, 47 (2014) 1-6. <https://doi.org/10.1186/1556-276X-9-47>
- [14] *E. Galeazzo, A. Beltran, F. J. Ramirez-Fernandez.* Natural Oxidation of Porous Silicon, *Brazilian Journal of Physics,* 27/ A, 4, (1997) 170-172.
- [15] *K.-H. Li, C. Tsai, J. Sarathy, J.C. Campbell.* Chemically induced shifts in the photoluminescence spectra of porous silicon. *Appl. Phys. Lett.* 62, 24 (1993) 3192-3194. <https://doi.org/10.1063/1.109126>
- [16] *K. Murakoshi, K. Uosaki.* X-ray photoelectron spectroscopic studies of the chemical nature of as-prepared and NaOH-treated porous silicon layer. *Appl. Phys. Lett.* 62, 14 (1993) 1676-1678. <https://doi.org/10.1063/1.109597>
- [17] *Y. Fukuda, W. Zhou, K. Furuya, H. Suzuki.* Photoluminescence change of as-prepared and aged porous silicon with NaOH treatment. *J. Electrochem. Soc.,* 146, 7 (1999) 2697 – 2701. <https://doi.org/10.1149/1.1391994>
- [18] *Y. Mo, A. Ren, J. Mao, Z. Zhou, H. Yuan, J. Du, D. Xiao.* Photoluminescence of oxidized porous silicon treated by sodium borohydride aqueous solution. *Materials Letters* 75 (2012) 115 – 117. <https://doi.org/10.1016/j.matlet.2012.01.130>
- [19] *F.A. Rustamov, N.H. Darvishov, V.E. Bagiev, M.Z. Mamedov, E.Y. Bobrova, H.O. Qafarova,* Influence of final treatment on the incubation period and antireflection properties of stain-etched porous silicon. *Phys. Status Solidi. A* 210, 10 (2013) 2174-2177. <https://doi.org/10.1002/pssa.201329298>
- [20] *F.A. Rustamov, N.H. Darvishov, M.Z. Mamedov, E.Y. Bobrova, H.O. Qafarova,* Formation of lateral homogeneous stain etched porous silicon with acetic acid at oxidant insufficiency, *Azerb. J. Physics.* 18, 3 (2012) 44-49. http://inis.iaea.org/search/search.aspx?orig_q=R_N:44023241
- [21] *G. Di Francia, A. Citarella.* Kinetic of the growth of chemically etched porous silicon. *J. Appl. Phys.* 77 (7) (1995) 3549–3552. <https://doi.org/10.1063/1.358585>
- [22] *F.A. Rustamov, N.H. Darvishov, V.E. Bagiev, M.Z. Mamedov, E.Y. Bobrova, H.O. Qafarova.* Determination of size and bandgap distributions of Si nanoparticles from photoluminescence excitation and emission spectra in n-type stain etched porous silicon, *J. Lumin.,* 154 (2014) 2024-2028. <https://doi.org/10.1016/j.jlumin.2014.04.037>
- [23] *X. Wen, P. Zhang, T.A. Smith, R.J. Anthony, U.R. Kortshagen, P. Yu, Y. Feng, S. Shrestha, G. Coniber, S. Huang.* Tunability limit of Photoluminescence in colloidal silicon nanocrystals. *Sci. Rep.* 5, (2015) 12469-12479. <https://doi.org/10.1038/srep12469>
- [24] *K. Dohnalova, A. Poddubny, A. Prokofiev, W. Boer, C. Umesh, J. Paulusse, H. Zuilhof, T. Gregorkiewicz.* Surface brightens up Si quantum dots: direct bandgap-like size-tunable emission. *Light Sci. Appl.* 2, e47 (2013); 1-6. <https://doi.org/10.1038/lsa.2013.3>

Received: 10.04.2023