

RED - YELLOW - RED REVERSIBLE SHIFT OF PHOTOLUMINESCENCE MAXIMUM IN STAIN ETCHED POROUS SILICON AT DILUTE HF POSTTREATMENT

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The effect of posttreatment in a diluted HF solution 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 $\sim 1.85\text{eV}$ to $\sim 2.1\text{eV}$. For posttreatment times less than 15min, subsequent atmospheric oxidation displaces the photoluminescence maximum again to 1.85eV , exhibiting a full red–yellow–red cycle. For posttreatment times more than 15min, subsequent atmospheric oxidation leads to photoluminescence quenching. The role of oxygen bonds in the observed phenomena is discussed.

Keywords: porous silicon; stain etching; posttreatment; diluted HF; yellow PL; oxygen bonds.

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1. INTRODUCTION

Since the discovery of the phenomenon of visible photoluminescence (PL) in porous silicon (PS), there has always been a question of tuning the position of its maximum [1, 2]. It would seem that the very reason that porous silicon, in contrast to bulk silicon, produces visible PL suggest such tuning method. Indeed, it is the phenomenon of quantum confinement that assumes the broadening of the bandgap of silicon nanocrystallites with a decrease in their size [1, 3–5]. Therefore, reducing the size of nanocrystallites during formation or postetching after formation, it is possible to increase the bandgap of nanocrystallites. However, in the experimental implementation of these methods, it turned out that in practice there is no significant shift of the PL maximum, despite the possible broadening of the bandgap [1, 4, 6, 7].

It is known that the position of the PL maximum and the size of silicon nanocrystallites during the electrochemical etching method depends on the type and value of the substrate conductivity, the composition of the solution, the current value, the duration of etching and illumination. In stain etching method, the PL peak position depends on the type and value of conductivity of the substrate, the composition of solution and the etching duration. But changing these etching conditions, affecting the intensity of the radiation, only leads to a slight shift of the PL peak position all PS samples obtained by conventional electrochemical or stain etching method and not subjected to additional postetching, regardless of their porosity, exhibit red or red-orange luminescence in air. The explanation for this fact lies in the oxidation of nanocrystallites, a theoretical basis is given in the works [3, 4]. In this work, it was theoretically shown that when hydrogen bonds Si – H are replaced by oxygen bonds Si–O, local levels appear in the PS bandgap. It is the appearance of these radiative register such a displacement, PS samples were kept and investigated in an argon atmosphere to prevent their

recombination levels that leads to red-orange photoluminescence regardless of the porosity and size of silicon nanocrystallites.

Oxygen bonds in the PS may occur at various stage of formation, according to the method of preparation. In the electrochemical etching method, the surface of as-prepared PS is covered with hydrogen bonds and they are replaced by oxygen bonds during subsequent exposure of the samples in air [8-10]. This oxidation, and hence the appearance of local radiation levels, occurs very quickly, during the first minutes of expose in air. Depending on the porosity of the samples, the existence of these levels manifests itself in different ways. As long as porosity of PS is low, the oxidation of nanocrystallites does not lead to the appearance of local levels in the bandgap, band-to-band transitions with red PL prevail. With an increase in porosity and a decrease in the size of Si nanocrystallites, the PL maximum shifts slightly to the high energy (orange) region. But if the porosity is high and the sizes of nanocrystallites are small ($\sim 2\text{nm}$), then this oxidation leads to the appearance of local levels of radiative recombination in the bandgap of PS. In this case, radiative recombination proceeds through these local levels, band-to-band transitions are not relevant, and such PS samples exhibit red-orange or orange photoluminescence. In this case, with an increase in porosity and a decrease in the size of nanocrystallites, the further shift to the high energy region is very insignificant [6, 7, 11].

For PS samples obtained by electrochemical etching, there are two possible ways of tuning the position of the PL maximum to the high energy region. In low porosity PS, regardless of the presence or absence of oxygen bands, postetching is required to reduce the size of nanocrystallites. And this is not a very convenient way. In works [1,4,12,13], such additional etching was carried out in hydrofluoric (HF) solutions with mandatory illumination for ~ 1 hour. In this case, the PL maximum shifted to the blue zone. To oxidation. When the sample was exposed to air, the PL maximum very quickly (1–3min) shifted back to the

red–orange region. Investigation of the *FTIR* spectra showed the correlation of this shift with the appearance of oxygen bonds when the samples were exposed to air. However, in highly porous samples with silicon nanocrystallites of about 2nm in size, additional postetching to reduce the size of nanocrystallites is not required. In this case, it is sufficient to remove the oxide layer, i.e. remove oxygen bonds which create local levels in the bandgap. Then the *PL* maximum should shift to the high–energy region. Unfortunately, such works are not found in the literature, which is apparently associated with the difficulty of obtaining highly porous *PS* samples by electrochemical etching without additional postetching.

In porous silicon obtained by chemical etching, the situation is somewhat different. These *PS* samples are usually highly porous, and oxygen bonds in them are formed already in the working solution [14-17], i.e. in the process of formation of porous silicon. That is, for the appearance of Si–O bonds and occurrence of radiative recombination local levels in the bandgap, atmospheric oxidation is not required. As a consequence, instead of the band-to-band transitions, transitions through these local levels immediately prevail here. Therefore, stain etched porous silicon, regardless of the porosity, immediately after preparation exhibits red – orange or orange *PL*. To shift the *PL* maximum in these *PS* samples, it is necessary to remove these oxygen bonds. As is known, oxygen bonds on the silicon surface are very easily and quickly removed with dilute 10% aqueous *HF* solution. But the effect of an aqueous *HF* solution, depending on the etching time, leads to both the removal of oxygen bonds and a further decrease in the size of silicon nanocrystallites. Therefore, the final result of the effect of posttreatment on *PL* requires further experimental research. In this work, we studied the effect of stain etched porous silicon posttreatment in a diluted aqueous – alcoholic *HF* solution on the *PL* spectra.

2. EXPERIMENT

Porous silicon samples were obtained by stain etching on monocrystalline silicon substrates of p- type polished on both sides, with a resistivity of 0.1 $\Omega\cdot\text{cm}$ 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 1min, and then in concentrated *HF* for 5min. The formation of *PS* layers was carried out at room temperature and daylight illumination in a $\text{HF}(50\%):\text{HNO}_3(65\%):\text{CH}_3\text{COOH}(\text{glacial})$ modified solution in volume proportion 1200:1:800, i.e. at oxidant insufficiency [18]. After the incubation time, the reaction of *PS* formation lasted 9 minutes. Such samples have a porosity of more than 70%, with crystallites size of 1.5÷2.8nm [16, 19, 20] (fig.1).

Some of the samples immediately after the formation of *PS* layers were washed in bidistilled water, then in isopropyl alcohol, and thereafter posttreated with a mixture of isopropyl alcohol and 10% aqueous *HF* solution (in a volume ratio 1:1) during 1÷60min. An alcoholic solution was used to increase the wettability of porous silicon. In all these procedures, it is important to prevent premature contact of the *PS* with atmospheric air. Then the samples were washed in bidistilled water, isopropyl alcohol and dried by N_2 jet. Immediately after drying, the *PL* spectra of the obtained samples were studied under ambient atmospheric conditions.

The *PL* spectra have been investigated under room temperature. The *PL* was excited by 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 320nm.

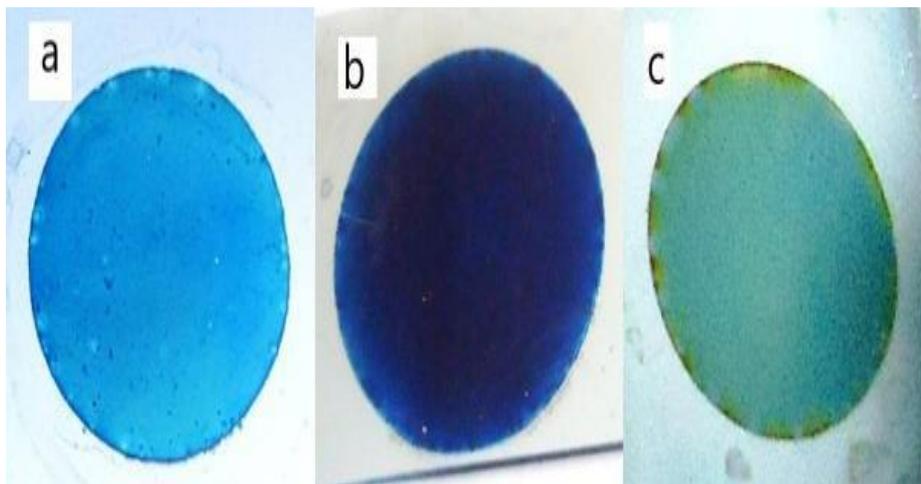


Fig.1. Stain etched *PS* layers formed in $\text{HF}:\text{HNO}_3:\text{CH}_3\text{COOH}$ solutions for a) 1.5min, b) 9min and c) 45min.

3. RESULTS

Fig.2 shows the photoluminescence spectra of stain etched PS samples both immediately after formation (a) and of PS samples immediately after posttreatment in an alcohol solution of 10% HF (b) at room temperature. As can be seen from the figure, these spectra are a strikingly different from each other.

The samples that have not undergone additional treatment exhibit red photoluminescence with a peak at $\sim 1.85\text{eV}$, and this maximum hardly shifts upon exposure to air (fig.2a). 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 1–15min immediately after formation exhibit yellow photoluminescence with a

maximum at 2.1eV (fig.2b). If the posttreatment of the samples was carried out for less than 15min, then upon contact the air their PL spectrum is transformed very quickly ($2\div 3\text{min}$) and the maximum shifts back to 1.85eV (fig.2 b-c transition). In this case, the PL spectra of untreated samples and samples posttreated in an alcohol solution of 10% HF and exposed in air for more than 5min practically coincide. Further exposure in air leads to a slight increase in the PL intensity without shifting its maximum (fig.2. c-d transition). If posttreatment in an alcohol solution of 10% HF lasts more than $\sim 15\text{min}$, the situation (PL behavior) changes somewhat. In this case, immediately after posttreatment, the samples also exhibit yellow PL with a peak at 2.1eV . But then, when exposed to air their PL is no longer shifted to the red region, and very quickly ($1\div 2\text{min}$) irreversibly quenched (fig.2 b-e transition).

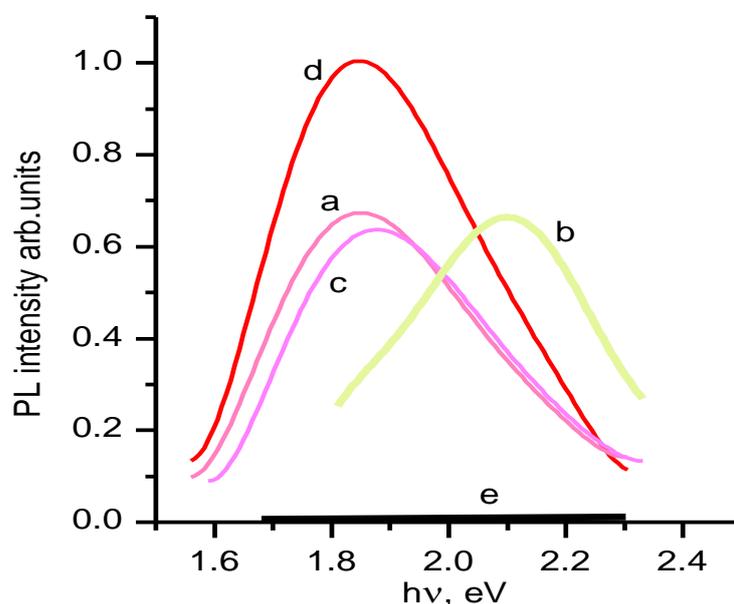


Fig.2. a) as-prepared PS without postetching; b) as-prepared PS postetched in dilute HF; c) postetched ($< 15\text{min}$) PS after 2min expose in air; d) postetched ($< 15\text{min}$) PS after 5min expose in air; e) PL quenching of postetched ($> 15\text{min}$) PS after 2min expose in air.

4. DISCUSSION

In fig.2a can be seen that porous silicon, immediately after formation by the chemical etching method, exhibits a red – orange (1.85eV) PL despite its high porosity. The position of this maximum is fairly stable and almost does not change at further atmospheric oxidation. Such stability of the PL spectra of stain etched PS distinguishes it from PS obtained by electrochemical etching [17, 21, 22]. Our earlier studies of the FTIR spectra [17] of such PS samples show that this fact is associated with the oxidation of silicon nanocrystallites (the band of 1108cm^{-1} corresponding to Si-O-Si asymmetric stretching of interstitial oxygen in Si and absorption peaks at 882cm^{-1} and 224cm^{-1} corresponding to $\text{O}_3\text{-Si-H}$ bending and stretching mode) already during the formation of PS in the etching solution (fig.3).

This fact distinguishes stain etched PS from samples obtained by electrochemical etching. That is, in these samples, local radiative recombination levels located in the bandgap and associated with Si-O bonds arise in the process of PS formation. Therefore, in spite of their high porosity and small size of silicon crystallites ($1.8\div 2.3\text{nm}$) [19, 20] these samples immediately after formation exhibit only red-orange PL.

As expected, the posttreatment of samples in a dilute HF solution immediately after formation led to significant shift of the PL maximum from 1.85eV to 2.1eV (fig.1, a-b transition). It is known that a dilute aqueous solution of HF very quickly removes the oxide layer on the silicon surface, what is widely used in silicon technology.

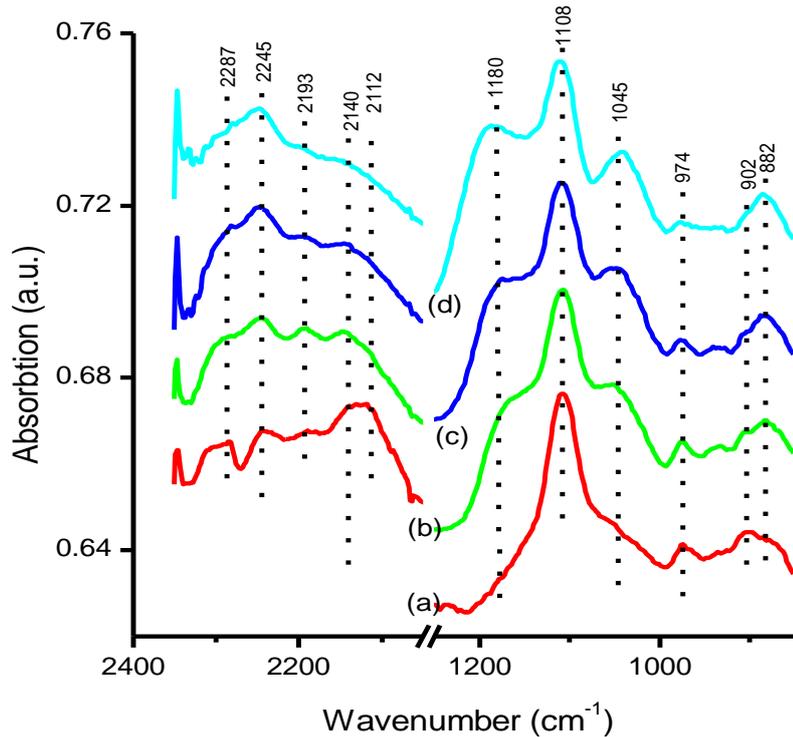


Fig.3. FTIR spectra of stain etched PS upon exposure to air: a) as-prepared, b) after 1 day, c) after 7 day, d) after 3 month.

In our case, such a treatment of the samples, by removing the Si–O bands, also leads to the removal of the local radiative levels associated with these bonds located in the bandgap of silicon nanocrystallites. Thus, the discrepancy between the small sizes of silicon crystallites and the position of the PL maximum is really associated with oxygen bonds, which in our case are formed during the formation of PS, namely, in the etching solution. But it should be noted that such a displacement can be detected only immediately after postetching PS in dilute HF, i.e. it is in freshly prepared samples, until it is affected by atmospheric oxidation.

Due to the high oxidizing ability of silicon, the situation changes after several minutes of exposure to atmospheric air. Depending on the posttreatment time in the HF solution, two radically different variants are observed. If the treatment time in the solution of HF is less than 15 minutes, then the PL maximum is reversed to the low energy region $\sim 1.8\text{eV}$ again (fig.2, *b–c* transition), i.e. the PL spectrum, which was observed before treatment in HF solution, is restored. This indicates the fact that when the treated samples are exposure in atmospheric air, silicon nanocrystallites are re-oxidized, which means that radiative recombination levels are again formed in the bandgap, leading to the observed shift of the PL peak. In terms of PL manifestation, a full cycle is formed: red–yellow–red. This once again prove the decisive role of Si–O bonds in the photoluminescence phenomenon manifested by silicon nanocrystallites in highly porous samples. On the other hand, this indicates that the posttreatment of freshly prepared PS samples in a dilute HF solution for less than 15min leads only to the removal of the oxide layer without changing the average size of Si

nanocrystallites. With further exposure to air, a certain increase in the PL intensity occurs at unchanged maximum position (fig.2, *c–d* transition). Such an increase in intensity is associated with additional oxidation of silicon particles in air (fig.3) (absorption peak at 1180cm^{-1} and 1045cm^{-1} , corresponding to Si–O–Si stretching LO and TO modes), resulting in better compensation for dangling bonds on the surface [17].

If the posttreatment time in diluted HF solution exceeds 15min, then, as in the previous case, yellow PL is first observed, but then exposure to air leads to the quenching of the visible PL (fig.2, *b–e* transition). In this case, the PL intensity during $2\div 3\text{min}$ drops to zero. Of course, this should also be connected with the oxidation of silicon nanocrystallites in atmospheric air. With an increase in the posttreatment time of freshly prepared PS samples in a dilute HF solution, not only the removal of the oxide layer occurs. Most likely, due to the long treatment time in HF, chemical etching of the nanocrystallites themselves begins to affect. In this case, the sizes of the crystallites are critically reduced. When such samples are exposure in air, their oxidation also occurs, but in this case, it is fully. This complete oxidation leads to the transformation of Si nanocrystallites into silicon oxide, and their ability to photoluminescence disappears.

5. CONCLUSION

The effect of posttreatment in a dilute aqueous HF solution on the photoluminescence of stain etched porous silicon has been investigated. The PS samples were obtained on the Si wafers by stain etching in a HF:HNO₃:CH₃COOH solution. Immediately after

formation, all PS samples exhibited red *PL* (~1.85eV) associated with oxygen bonds formed directly in the etching solution during formation. All samples were subjected to posttreatment in a dilute *HF* solution for various time. It was revealed that such posttreatment of the investigated samples always leads to a shift in the maximum of their *PL* from the red (~1.85) to the yellow (~ 2.1eV). This shift is associated with the removal of oxide layers on the surface of Si nanocrystallites, which led to the formation of radiative recombination levels in the bandgap and was the cause of the red *PL* regardless of the size of the nanocrystallites. When exposed to air, due to atmospheric oxidation, the *PL* spectra transformed within 2÷3min. If posttreatment

time was less than 15min, then the *PL* maximum shifted again to the red region, completing the red–yellow–red cycle. This shift is associated with the repeated formation of oxygen bonds on the surface of nanocrystallites. If the posttreatment time was more than 15min, then the yellow *PL* was extinguished. This is due to the fact that, at long postetching times in *HF* solutions, etching of the silicon crystallites themselves begins to affect. In this case, the size of the nanocrystallites decreases critically, and when they are exposed in air, they are completely oxidized, transforming into silicon oxide, and the ability to *PL* disappears.

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