Post-anodic formation of luminescent porous silicon layers in atmospheric environment

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The changes occuring in HF pre-etched porous silicon (PS) samples during aging are studied by measurement of photoluminescence (PL) and IR transmission spectra. The PL behavior of the etched sample is found to depend on the time of PS pre-exposure to the air after anodizing and, hence, on the initial luminescence quantum yield. The results are explained by the PS structure modification during the etching and oxidation of the samples.

С помощью спектроскопии фотолюминесценции (ФЛ) и ИК поглощения исследовались изменения, происходящие в процессе старения травленных в HF образцов пористого кремния (ПК). Поведение ФЛ травленных образцов зависит от длительности предварительного экспонирования ПК на воздухе после анодирования и, соответствено, начального квантового выхода люминесценции. Полученные результаты объясняются модификацией структуры ПК в процессе травления и окисления образцов.

The unique environment sensitivity of chemical, electrical, optical and especially luminescent properties is a characteristic feature of porous silicon (PS). On the one hand, such a feature hampers the practical use of PS in light-emitting devices due to its instability in air [1, 2]. On the other hand, this feature makes it possible to control the PS luminescent properties [3, 4]. Investigations in this direction can be useful to identify the luminescence mechanism. Study of chemical treatment effect on the PS evolution process in the ambient atmosphere can also be of interest.

The as-anodized PS samples were shown [2, 5] to have a small quantum yield of photoluminescence (PL). Storing the samples in the air results in a progressive oxidation of PS and increase in their PL intensity. Notable changes in the PS sample occur in the atmospheric environment for several months, its PL intensity rising. The oxidation rate and final PL characteristics depend on preparation conditions, the sample washing and drying methods. Evolution of luminescent properties and chemical composition of HF pre-treated samples stored in the ambient atmosphere has been studied in this work.

Two types of samples were studied. The first are the samples with low initial quantum yield which were held in the ambient atmosphere for a short time after preparation, and the second are the samples with efficient PL where the natural oxidation has been completed.

The PS samples were obtained by electrolytic anodizing the (111) boron doped p-Si wafers in 48 % HF and isopropyl alcohol (1:1) solution at the current of 10 (samples A and A′) and 20 mA/cm^2 (sample B) for 5 min. After anodizing, the sample A was stored for 2 months in the ambient atmosphere. The samples A′ and B were exposed to air for one year, their luminescent properties were stabilized during this storage. The samples A and B were further subjected to HF chemical treatment for 3 min and 20 seconds respectively, and thereafter
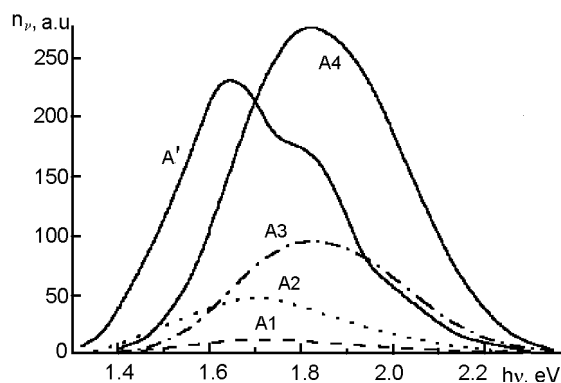
Fig. 1. PL spectra evolution during storage of the samples A and A′ in ambient atmosphere without HF treatment (A1, A′) and 5 min (A2), 7 days (A3), 60 days (A4) after HF etching.
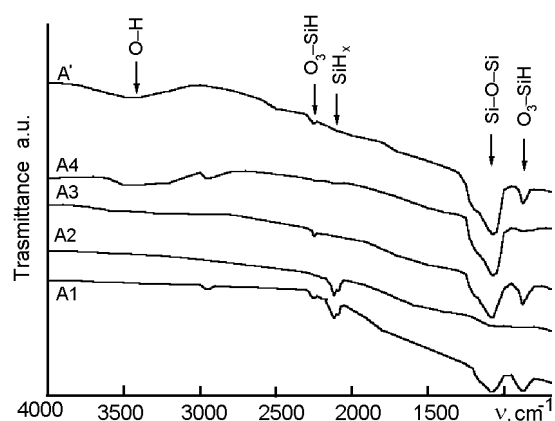

Fig. 2. PS sample IR transmission spectra corresponding to those in Fig. 1. Spectrum A2 is measured 1 h after the chemical treatment.

were washed in CCl_4. After the treatment, the samples were exposed to air for 60 days, the PL intensity of sample A peaked for this time (PL efficiency was almost unchanged for longer storage time).

The visible PL spectra were measured at room temperature, an ILGI-503 nitrogen pulsed laser (337 nm) was used for excitation. IR absorption spectroscopy was used to investigate silicon surface bonds with oxygen and hydrogen. The IR transmission spectra were measured at room temperature by a Specord IR-75 two-beam spectrophotometer in the 400 to 4000 cm^{-1} range.

In the experiment, it was noted that a red shift occurs in PL spectrum of A-type PS sample as a result of HF treatment and the PL intensity increases substantially. Further, the spectrum shifts rapidly towards higher energies, the luminescence intensity slightly decreases for the first minutes and thereafter starts to rise. These data agree with those published before [6]. The PL spectra of sample A for different stages of the intensity rise are presented in Fig. 1. During 7 days, the spectrum peak was shifted from 1.7 to 1.83 eV (curve A3). The further storage in the air results only in an increase of the sample quantum yield. Already after 2 months of aging, the luminescence efficiency exceeded that of the untreated sample stored in the air for more than a year (curve A′). The structure of this curve is caused by interference.

Before the HF treatment, the absorption bands at 2090–2135 cm^{-1} caused by $Si-H_x$ vibrational modes (x = 1–3), the wide band between 1070 and 1200 cm^{-1} caused by Si–O–Si bonds mode as well as two lines at

875 and 2250 cm^{-1} of the vibrational modes of Si–H bonds in O_3–SiH species [7, 8] are observed in the IR transmission spectrum of sample A (Fig. 2). The HF treatment of the sample has resulted in almost complete vanishing of the absorption bands caused by vibration of the silicon-oxygen bonds from the spectrum. During several next days, the substitution of hydrogen coating by oxygen one takes place as well as oxidation of so-called "back bonds", and the bands caused by vibration of the Si–H bonds in the O_3–SiH species are observed in the spectrum of the sample which was stored for 7 days in air after the chemical treatment. It should be noted that the sample oxidation occurs quickly during the first days after etching. Intensity of the band at 1070–1200 cm^{-1} has increased essentially during this period. At the next stage, the oxygen content in the sample rised more slowly. The IR transmission spectra of the completely aged samples without HF treatment (A′) differ from those of HF treated ones (A4) only in the presence of O_3–SiH caused bands. In the second ones, these bands were completely disappeared. A wide low-intensity band at 3000–3800 cm^{-1} which is related to O–H bond vibration in H_2O or SiOH molecules adsorbed on the surface [8] is observed in both spectra.

Effect of chemical treatment on the PL of sample B which has effecient luminescence due to prolonged pre-storage in air differs from that on sample A with low initial quantum yield. Even a short-time (10 s) HF treatment of sample B results in a significant decrease in PL intensity (by a factor of nearly 200). The PL intensity rises very rapidly during first few minutes when
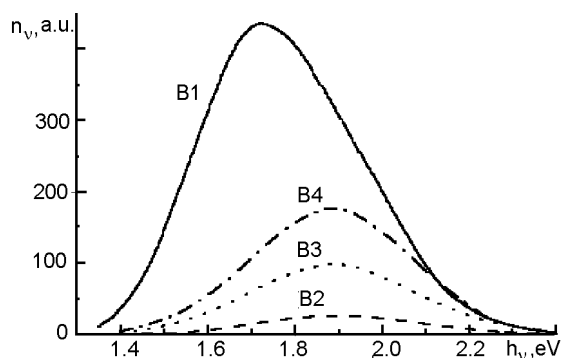
Fig. 3. PL spectra of sample B before (B1) and after HF etching, the sample being exposed to air for 5 min (B2), 7 days (B3), 60 days (B4).

exposing to air and the peak shifts quickly towards higher energies. The spectrum evolution slows down after 10 minutes, no essential shift of the maximum occurs during further aging, and PL quantum yield of the sample increases gradually, although the value before chemical treatment is not restored (Fig. 3).

Only intense Si–O–Si and O_3–SiH bands were observed before the etching in the IR transmission spectrum of sample B (Fig. 4, curve B1). As a result of the chemical treatment, the hydrogen bands appear in the spectrum and intensity of the oxygen bands essentially drops. The further spectrum evolution progresses during the sample aging essentially in the same manner as for sample A (see Fig. 2).

The porous layer of as-anodized sample is known to be structurally inhomogeneous in the depth [9]. A film of so-called contaminated oxide, i.e., SiO_x compound with C, H, OH group impurities [10] is formed in the porous layer during oxidation. The oxidation progresses more rapidly in the near-surface region of a sample [11], the nanostructure sizes decreasing and even fragments being separated from the silicon skeleton by oxide layer. The oxidation in deeper PS layers is not so efficient, the sizes of silicon structure are larger, its surface is probably passivated with both oxygen and, to an appreciable extent, with hydrogen. There is a high concentration of silicon dangling bonds at these depths, which are known to be centers of non-radiative recombination [9]. The visible PL of such samples can be considered as the band-to-band luminescence of silicon nanostructures where the bandgap is enlarged due to the quantum-size effect.
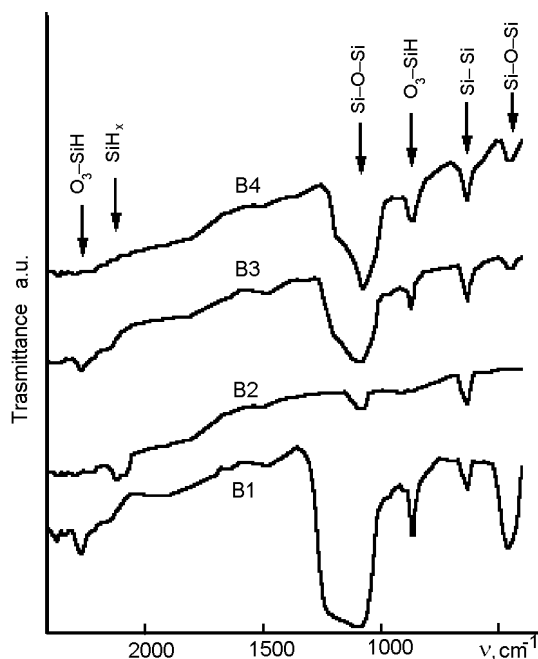

Fig. 4. Sample B IR transmission spectra which correspond to those presented in Fig. 3. Spectrum B2 is measured 1 h after the chemical treatment.

When etching sample A in HF, dissolution of the surface oxide layer and passivation of the silicon dangling bonds with hydrogen occur. Just after etching, the PL intensity increases as compared to that of untreated sample due to decreased number of non-radiative recombination centers. The red shift occurs due to a greater contribution to PL of the larger nanofragments where the suppression of non-radiative surface recombination channel manifests itself more effectively at passivation [12]. Furthermore, the small-sized silicon nanocrystallites separated by oxide are washed out of the sample when dissolving the oxide layer.

The silicon dangling bonds are generated again during the first minutes of PS exposure to air, hydrogen desorption probably runs more rapidly than surface saturation with oxygen [11]. This results in some PL intensity drop and the spectrum peak shift towards higher energies. The further oxidation causes a better passivation of the surface as well as the nanostructure size reduction accompanied by a rise of the PL quantum yield and the spectrum shift toward shorter waves. It should be noted that silicon oxide is believed to be the luminescence sensitizer, therefore, increase in its content alone must enhance the luminescence intensity.

As the oxide layer is built up on the silicon skeleton, the oxidation is slowed down gradually. Change of the PL spectrum peak position is no longer to be observed, although reduction of the crystallite size must occur at this stage as well. This provides reason to suppose formation of another channel of radiative recombination. So, it was noted [13] that the Si=O double bonds are generated at the Si/SiO$_2$ interface during oxidation, thus resulting in appearance of new electron states in the small crystallite bandgap. Radiative recombination can occur through these states. The luminescence in the small crystallites is an intracenter one, and its spectrum does not essentially depend on the nanocrystallite size.

The spectrum of aged etched sample (see Fig. 3, curve B4) is shifted towards higher energies as compared to that of non-etched sample. This can be explained by different sizes of crystallites in these samples. The etched sample obviously has a smaller-sized nanostructure. This can be caused by oxide building up during the preliminary aging. This oxide is removed during HF etching. It is just the already thinned structure that is further subjected to oxidization.

It should be noted that the chemical treatment accelerates significantly the oxidation of porous layer and, respectively, enhancement of its PL intensity. It causes etching the contaminated oxide film off the sample surface, resulting in an enlargement of voids between the nanostructure elements as well as cracking the PS layer. As a result, air penetration deep into the sample is facilitated.

The HF chemical treatment of sample B results in destruction the oxidized layer structure. The PL intensity drops significantly due to removal of large number of the separated crystallites which were immersed in the oxide compound and emitted efficiently. The subsequent aging occurs essentially in the same manner as for sample A but noticeably faster because the pores were considerably enlarged due to the pre-oxidation. However, the final efficiency is much lower than the initial one because of the large amount of the material removed by the etching.

So, the prolonged exposure of the sample to air makes it possible to obtain the PS layers with a high quantum yield of PL which can attain 0.2 [11]. The natural PS oxidation is a prolonged and irreproducible process that can be substituted by other, more technological methods as well. How-ever, each of those has drawbacks. Thus, the anodic oxidation is performed to the stage when the drastic rise of sample resistance begins, which is interpreted as the local separation of silicon quantum wires with oxide [3, 14]. The oxidation process occurs non-uniformly over the sample depth, i.e., the oxygen content is the maximum in the PS interlayer adjacent to the substrate. The main part of the porous layer is not completely oxidized. The rapid thermal oxidation [15] is performed by exposing the PS samples to the oxygen atmosphere at high temperatures. However, vacuum annealing of the sample at temperatures exceeding 450°C affects negatively and irreversibly the luminescence intensity because the porous structure is modified [16]. Of course, the oxide coating formed at high temperatures (up to 1000°C) at the nanostructure surface is likely to hinder the modifications. However, the negative action of high temperatures on the luminescence obviously takes place in this case, as well, because researchers report only two or three times rise of the PL intensity as compared to the as-prepared sample. The chemical oxidation of PS by immersing the sample in H$_2$SO$_4$ allowed to increase twice the PL intensity [5]. However, the acid treatment causes cracking and destruction of the porous layer [17].

The natural oxidation of PS by exposing the samples to air is free of drawbacks inherent in the artificial methods, although it has its own limitation: saturation of PS by oxygen is inhomogeneous over the layer thickness due to small sizes of the pores through which the atmospheric components penetrate deep into PS. The air penetration deep into porous layer can be promoted by a short-time acid etching of the sample, what eventually makes it possible to obtain the samples with high PL quantum yield. Such a technique can be suggested as a method to enhance the PL efficiency.

Thus, the HF etching effect on the evolution of PS sample luminescent properties in air depends on the aging stage whereat the chemical treatment of sample is carried out. The difference is due to the structure features of the studied samples which are due to different oxidation degrees. The luminescence of the PS samples untreated in HF is considered to be the band-to-band PL of quantum-size silicon, whereas PL of the etched samples is related to the surface electron states formed as a result of the sample oxidation.

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Післяанодне формування люмінесцентних шарів поруватого кремнію в умовах атмосферного оточення

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За допомогою спектроскопії фотолюмінесценції (ФЛ) та ІЧ поглинання досліджувалися зміни, що відбуваються у процесі старіння травлених у HF зразків поруватого кремнію (ПК). Поведінка ФЛ зразків, що травилися, залежить від тривалості попереднього експонування ПК на повітрі після анодування і, відповідно, початкового квантового виходу люмінесценції. Отримані результати пояснюються модифікацією структури ПК протягом травлення та окислення зразків.