INFLUENCE OF THE HF VAPOR TREATMENT ON THE STRUCTURE AND LUMINESCENCE PROPERTIES OF POROUS Si/SiO$_x$ NANOCOMPOSITES

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By methods of IR-spectroscopy and photoluminescence, we studied the influence of the etching of the oxide matrix of porous nanocomposite Si/SiO$_x$ structures by HF vapors. The structures were produced by the thermal deposition (TD) of silicon monooxide in vacuum at an angle of 60° on c-Si substrates with the subsequent annealing at 975 °C. It is shown that the treatment in HF vapors causes a significant decrease in the volume of a film and a partial additional oxidation of its surface, as well as to the appearance of complexes O_3SiH and O_2SiF_2 in the film. On the surface of silicon nanoinclusions, complexes Si_3SiF arise. Simultaneously, an essential (up to 210 nm) shift of the emission maximum from the infrared range to the visible one of the spectrum and a significant (up to 200 times) increase in the luminescence intensity are observed. These effects can be explained by the process of modification of a structural impurity-involved state of the nanoinclusion-Si–SiO$_x$ interface as a result of the action of an etcher on a porous film. The light emission intensity grows due to the passivation of broken bonds of silicon on the nanoinclusion-Si–SiO$_x$ interface by atoms of oxygen and fluorine. The oxidation of the surface of silicon nanoinclusions decreases their size, which is revealed in a short-wave shift of photoluminescence (PL) spectra.

1. Introduction

Nanocomposite structures Si/SiO$_2$ (silicon nanoparticles built-in into a film matrix of silicon oxide SiO$_2$) are widely studied due to their prospects for the development of a new generation of light-emitting devices and memory units on the basis of quantum dots of silicon [1-5]. The emission of silicon nanoparticles in SiO$_2$ occurs in the red and near IR-ranges of the spectrum and is characterized by a rather low intensity due to the presence of a large number of centers of nonradiative recombination on the nc-Si–SiO$_2$ interface [6]. A decrease in the concentration of these centers can be attained, in particular, by the passivation of the surface of nc-Si by hydrogen [6]. However, the emission intensity significantly decreases again in the course of time, which is related to the desorption of hydrogen atoms from the surface of specimens [7], especially under the action of UV radiation which destroys weak Si–H bonds. It is also known [8] that the chemical treatment in a solution of hydrofluoric acid of continuous SiO$_2$ films which contain nc-Si leads to a significant increase in the intensity of red photoluminescence which does not vary for a year. This effect was explained by the selective dissolution of the SiO$_2$ phase around silicon nanoparticles in HF and by the subsequent reaction of hydrogen atoms and oxygen of the etcher with broken bonds of silicon. This results in the formation of Si=H$_2$ and Si=O$_2$ bonds, by passivating the nc-Si surface in such a way. In our previous works [9–10], we showed that the etching of porous thin-film nanoinclusion-Si/SiO$_x$ structures in a dilute (1%) solution of HF also changes essentially the luminescence properties of these structures:
– the emission intensity increases significantly due to the passivation of nonradiative recombination centers on the surface of Si-nanoinclusions, and the spectrum composition of the emission is changed due to a decrease in the size of nc-Si. However, the etching of porous films in a fluid leads to a partial transfer of Si nanoparticles into the solution, which decreases the luminescence intensity. On the other hand, it is known that the recombination activity of the surface of silicon is essentially decreased at its treatment in HF vapors [11]. Therefore, the present work continues the study of the influence of a chemical treatment on the structural and luminescent properties of porous nanoinclusion-Si/SiO$_x$ systems with the use of the etching in HF vapors.

2. Experimental Procedure

Thin (850±30 nm) porous films of SiO$_x$ were produced by the thermal evaporation of silicon monooxide SiO of the Cerac firm with the 99.9-% purity in vacuum (1–2×10^{-3} Pa) on Si substrates (100) which were polished on both sides and placed at an angle of 60° be-

tween the normal to the substrate surface and the direction to an evaporator. The produced films were annealed for 15 min in a vacuum chamber at a residual pressure of 1×10^{-3} Pa and a temperature of 975 °C. As a result, SiO_x was decomposed into silicon nanoparticles and silicon oxide. The earlier executed studies of a structure of sprayed films of SiO_x with the help of a high-resolution electron microscope ZEISS EVO 50XVP showed that the as-produced films have a porous column-like structure, where the diameter of columns varies in the limits 10–100 nm [12–13]. The size of columns, their orientation, and the porosity of a structure depend on the film deposition angle. The porosity of specimens deposited at an angle of 60° was determined in [12] and was equal to 34%. After the high-temperature annealing of films, the porosity, size, and orientation of columns remain unvariable.

The etching of annealed nanoinclusion-Si/SiO_x specimens was carried out in a hermetic box, in which saturated HF vapors possess a temperature of 30 °C. Vapors of hydrofluoric acid manifest a selective action on the film under study, i.e., they etch silicon oxide, by forming gas-like radicals of the SiF_4 type, and do not interact with silicon.

IR-transmission spectra were measured by a Fourier spectrometer Spectrum BXII PerkinElmer. A substrate made of single-crystal silicon (without an oxide film) serves a reference specimen. By positions of the maxima of transmission bands, we identified the presence and the kind of chemical bonds. The composition of the SiO_x matrix (with the stoichiometry index x) was determined by the absorption band maximum position for Si–O bonds (the maximum in the interval 1000–1100 cm^{-1} depending on a value of the stoichiometry index) from the available dependence [14] for oxide films produced by the thermal evaporation. In order to determine structural elements of the oxide matrix [the type and a relative contribution of molecular complexes SiO_ySi_{4-y} ($1 \le y \le 4$)], the spectra of the optical density were decomposed into elementary components of the Gauss shape which were analyzed by the earlier proposed method [15, 16].

The measurement of PL spectra was carried out at room temperature. The spectral composition of the emission was analyzed with a monochromator ZMR-2 and was registered with photomultipliers FEP-51 and FEP-62 cooled with liquid nitrogen. PL was excited by the radiation of a pulsed nitrogen laser at a wavelength of 337 nm. As for PL spectra, we took the spectral sensitivity of the measuring setup into account.

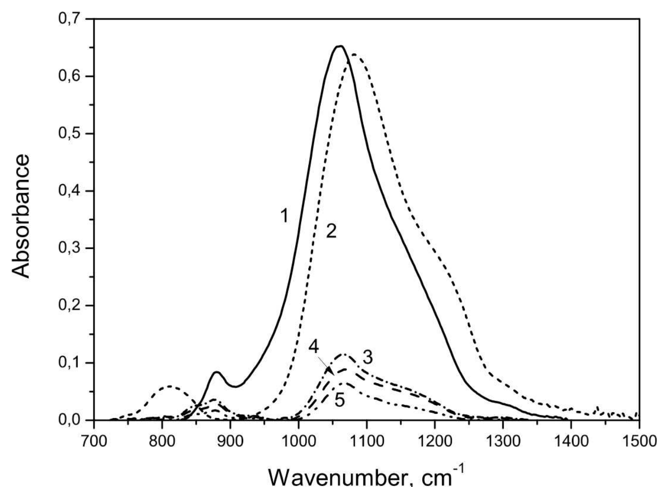


Fig. 1. IR-absorption spectra of porous nanocomposite Si/SiO_x films in the interval 700–1500 cm^{-1}: before annealing (*1*), after annealing (*2*), and after the etching in HF vapors for 1.5 (*3*), 10 (*4*), and 30 (*5*) min

3. Results and Their Discussion

3.1. IR-Spectroscopy

In Fig. 1, we show the absorption spectra of specimens under study in the region 700–1400 cm^{-1}. The basic absorption band (on valence asymmetric oscillations of oxygen atoms in "bridges" Si–O–Si) of the as-produced (prior to the annealing) film is inherent by its position (1062 cm^{-1}) to a nonstoichiometric silicon oxide with $x \approx 1.73$ [14], which corresponds completely to conditions of the deposition of the film. Its decomposition into elementary components (see Tables 1 and 2) demonstrates that the structure of the as-produced porous film is described within the model of random coupling as a mixture of molecular complexes SiO_ySi_{4-y} ($1 \le y \le 4$). In addition to Gaussians inherent to molecular silicon-oxygen complexes, the decomposition contains also the component with a maximum at $\sim$940 cm^{-1} which is usually referred to hydroxyl complexes SiOH [17].

In addition to the basic absorption band, we observe also a band at $\sim$878 cm^{-1} in the above-mentioned spectral range (Fig. 2, Table 1) which can be assigned to the absorption on deformational (scissors) oscillations of hydrogen in Si-H complexes [17, 18]. The presence of silicon hydrides in the as-produced film is confirmed also by the results of measurements in the region 2000–2400 cm^{-1} (Fig. 3, Table 1) containing the bands of absorption on valence oscillations of hydrogen atoms in Si-H complexes with different local configurations which are located in the oxide matrix [17, 19]. Here, a doublet

T a b l e 1. Vibration frequencies and the nature of IR-absorption bands

Si–O mode		Impurity modes	
Frequency (cm^{-1})	Structural configuration	Frequency (cm^{-1})	Structural configuration
810 (symmetric)	SiO_4	845	Si_3SiF
1000	$SiOSi_3$	878 (deformational)	O_3SiH
1032	SiO_2Si_2	920	O_2SiF_2
1054	SiO_4(4-membered rings)	940	SiOH
1068	SiO_3Si	2155	O_2SiH_2 or OSi_2H_2
1090	SiO_4 (6-membered rings)	2255 (valence)	O_3SiH
1140	SiO_4(linear fragments)		

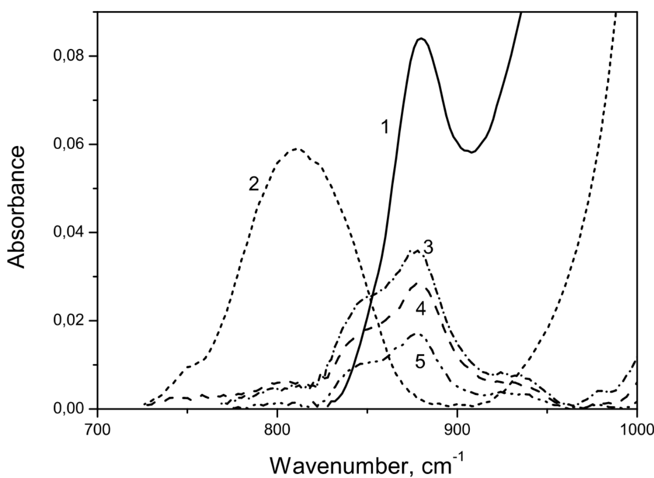


Fig. 2. Enlarged view of IR-absorption bands of porous nanocomposite Si/SiO_x films in the interval 700–1000 cm^{-1}: before annealing (*1*), after annealing (*2*) and after the etching in HF vapors for 1.5 (*3*), 10 (*4*), and 30 (*5*) min

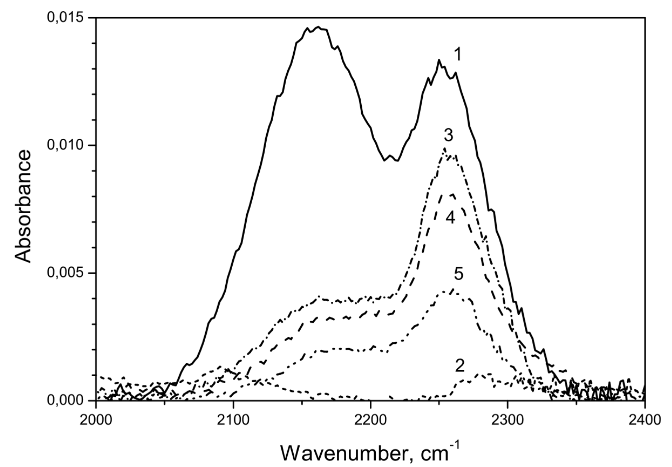


Fig. 3. IR-absorption spectra of porous nanocomposite Si/SiO_x films in the interval 2000–2400 cm^{-1}: before annealing (*1*), after annealing (*2*) and after the etching in HF vapors for 1.5 (*3*), 10 (*4*), and 30 (*5*) min

with absorption maxima at ~2160 and ~2255 cm^{-1} is clearly observed. The nature of the first band is related to silicon oxyhydrides, whose composition includes two hydrogen atoms [19, 20], though different viewpoints on their structural configuration are known: it can consists of complexes O_2SiH_2 [20] or complexes OSi_2H_2 [19]. The nature of the band at ~2255 cm^{-1} is uniquely related to O_3SiH complexes [17-20]. Moreover, it is considered that the given structural element corresponds also to the above-mentioned peak at ~878 cm^{-1} in the region of deformational oscillations [19].

Thus, the structure of as-produced porous films of SiO_x can be described as a mixture of silicon-oxygen tetrahedra with different degrees of oxidation of silicon. A part of silicon and oxygen bonds ios saturated by hydroxyl groups and hydrogen atoms, which is related, most likely, to the presence of water vapors in the atmosphere of residual gases at the deposition of the film.

The subsequent high-temperature annealing leads to the basic changes in IR-absorption spectra (Figs. 1–3). First, we observe a shift of the basic absorption band to the high-frequency region (the peak at 1082 cm^{-1}), some increase (by ~8%) in the area of the band related to Si–O–Si oscillations, and a change in the band shape. Second, a rather intense band with maximum at ~810 cm^{-1} appears in the spectra of annealed specimens. Third, all bands related to hydroxyls and hydrogen disappear.

Two first facts testify that the annealing results in the thermostimulated decomposition of oxide accompanied

T a b l e 2. Share of bands of the absorption by valence oscillations of oxygen atoms in different structural configurations

Specimen	Share of the absorption band in TD mode, %			
	$Si–O–Si_3$	$Si–O_2–Si_2$	$Si–O_3–Si$	$Si–O_4$
As-produced	18.1	25.4	28.6	27.9
Annealed	5.9	6.8	7.0	80.3
Etched in HF for 1.5 min	0.0	18.1	30.9	51.0
Etched in HF for 10 min	0.0	13.0	32.1	54.9
Etched in HF for 30 min	0.0	10.7	40.1	49.2

by the formation of an oxide matrix with a high stoichiometry index ($x \approx 1.97$ [14]), decreases the number of broken bonds Si-O-Si, and changes a structural state of oxygen in a film. According to the decomposition results, the structural lattice of an annealed film contains a significant part of tetrahedra SiO_4 which form interconnected 4- and 6-membered rings and linear fragments. The film contains also a cetain amount of incompletely oxidized silicon complexes $SiOSi_3$, SiO_2Si_2, and SiO_3Si (see Table 1). Thus, the annealed oxide structure can be considered as a mixture of the phases SiO_2 and SiO_X. The presence of the developed phase SiO_2 is supported by the appearance of a band at $\sim$810 cm^{-1} which is inherent namely to silicon dioxide and is related to valence symmetric oscillations of oxygen atoms [14, 21]. The disappearance of silicon hydrate and hydride groups is obviously related to the desorption of hydroxyls and hydrogen atoms from a porous film as a result of the high-temperature treatment in vacuum.

The subsequent etching of annealed specimens causes the significant reduction of the IR-absorption, whose degree correlates with the duration of the treatment in HF vapors. This fact is related to a decrease in the volume of a porous film. Simultaneously, the basic absorption band (Fig. 1) shifts to the low-frequency region (the peak at $\sim$1068 cm^{-1}), i.e., the stoichiometry index of the oxide ($x \approx 1.81$ [14]) decreases (as compared with that of an annealed specimen) due to the etching. The absorption bands of etched specimens are decomposed into Gaussians which are related to the absorption of the SiO_x phase (see Table 2). In other words, the etched films have the composition and the structure of the nonstiochiometric silicon oxide. The last fact is confirmed also by the disappearance of the band at $\sim$810 cm^{-1}.

At the same time, the absorption bands in the intervals 800–1000 cm^{-1} and 2000–2400 cm^{-1} arise again in the spectra of films treated in the etcher (Figs. 2 and 3), but with a somewhat modified shape as compared with that of the spectra of as-produced specimens. The band with a peak at $\sim$878 cm^{-1} is considerably widened and becomes asymmetric: it can be represented as a superposition of a band at $\sim$878 cm^{-1} and two ones (less intense) at $\sim$845 and $\sim$920 cm^{-1} (Table 1). Just such a triplet was observed in the nc-Si/SiO_x systems treated with a plasma containing SF_6 [20]. The nature of the band at $\sim$920 cm^{-1} which is new in the measured spectra is assigned to symmetric valence oscillations in complexes O_2SiF_2 [20, 22], whereas the bands near $\sim$845 cm^{-1} are referred to deformational oscillations of hydrogen in hydride complexes [20] and to valence oscillations of Si–F [22]. In view of the fact that, in the last case, the mentioned band was observed in films of amorphous silicon doped by fluorine (no hydrogen was present), we may consider that the band at $\sim$843 cm^{-1} in the specimens under study is most probably related to namely complexes Si-F localized on the surface of silicon nanoinclusions.

The etching induces the redistribution of the intensities of the bands at 2160 and 2255 cm^{-1} (as compared with the as-produced specimen). The latter dominates, i.e., the film contains mainly complexes O_3SiH. We note that the indicated changes occur already at the first stage (1.5 min) of the treatment of films, and then they are qualitatively retained.

The results obtained can be explained by the dissolution of the regions with the SiO_2 phase as a result of the treatment of porous films in HF vapors, so that only the SiO_x phase remain in the film. Such an etching of the silicon dioxide phase already at the first stage of the treatment is possible only if this phase is at once in contact with the etcher. This can mean that the mixture of the SiO_2 and SiO_x phase in an annealed porous film has no chaotic character. Most likely, the SiO_x phase is in the core of columns which are covered by a shell consisting of the SiO_2 phase.

The further treatment in vapors of the etcher continues to decrease (though to a much less extent) the intensity of the absorption by Si–O bonds (see Fig. 1). This result can be explained by the following. In the process of action of vapors of the etcher on a porous film which is composed already of SiO_x columns after the first stage of the etching, the surface of columns is additionally oxidized to the SiO_2 state under the action of air. The formed surface superthin layer of silicon dioxide is dissolved by HF vapors, and a further reduction of the silicon-oxygen phase volume occurs. The additional oxidation of the film in the process of etching is directly confirmed by the results of measurements of IR-spectra. It is seen from data presented in Table 1 that molecular complexes $SiOSi_3$ disappear from the film in the process of treatment in HF vapors. Moreover, the content of complexes SiO_2Si_2 decreases, whereas the content of complexes SiO_3Si, on the contrary, increases. In other words, poorly oxidized silicon-oxygen complexes are transformed into highly oxidized ones under the action of air. In addition, the appearance of the surface layer SiO_2 (or SiO_x with x close to 2) is confirmed also by the fact that, according to the statistics of the model of random coupling, complexes O_3SiH formed on the surface of columns due to the interaction of silicon oxide

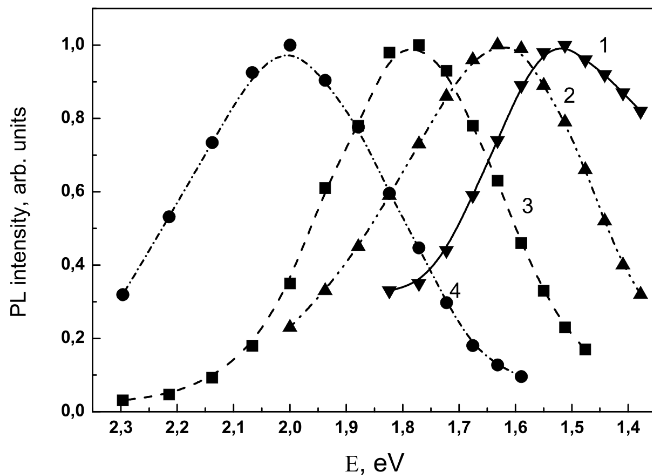


Fig. 4. Normalized PL spectra of an annealed porous nanocomposite Si/SiO_x film before (curve *1*) and after the etching in HF vapors for 1.5 (*2*), 10 (*3*), and 30 (*4*) min

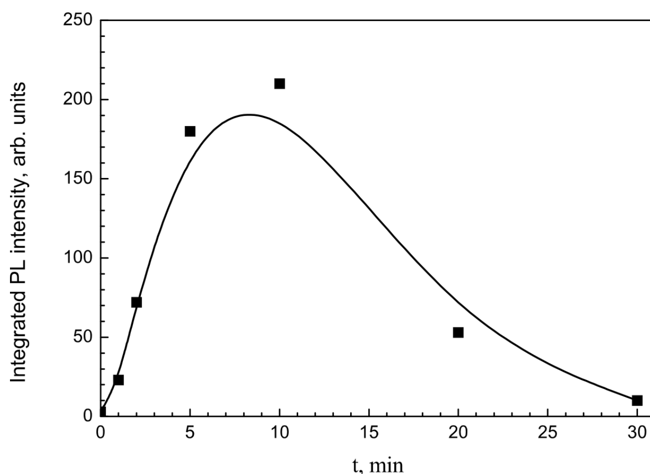


Fig. 5. Integral PL intensity of nanoinclusions Si in porous nanocomposite Si/SiO_x films versus the etching duration

with the etcher are characteristic of oxides with a high content of tetrahedra SiO_3Si or SiO_4, i.e., with a large value of the stoichiometry index [18].

3.2. Photoluminescence

In Fig. 4, we show the normalized PL spectra of Si/SiO_x nanocomposite specimens annealed at 975 °C (curve *1*) and treated after the annealing by HF vapors for 1.5, 10, and 30 min (curves *2*, *3*, and *4*, respectively). The emission spectrum of the annealed specimen is described by a single wide PL band in the IR region of the spectrum with a maximum near 830 nm. This band has a low intensity, which is caused by a great number of defects such

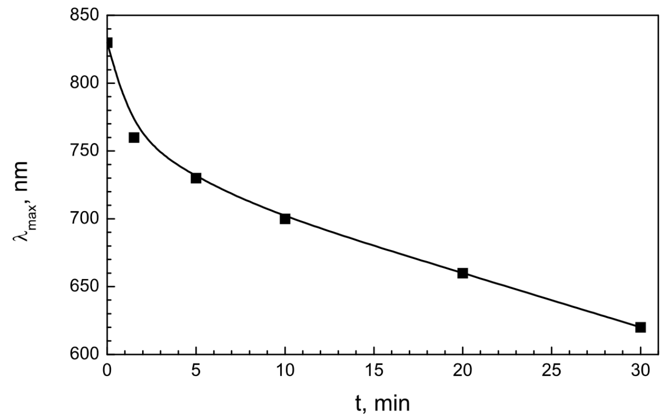


Fig. 6. Positions of the PL maxima of Si nanoinclusions in porous nanocomposite Si/SiO_x films versus the etching duration

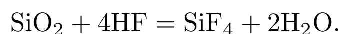
as broken bonds of silicon on the surface of Si nanoinclusions which serve the centers of nonradiative recombination [23]. In the literature, this band is referred to the radiative recombination of electron-hole pairs coupled into excitons which are excited on separate silicon nanoparticles surrounded by the oxide matrix [24].

The treatment of specimens in HF vapors causes the essential changes in the emission spectrum. First, the PL intensity grows strongly (up to 200 times) (Fig. 5). Second, a shift of the emission spectrum to the short-wave side is observed in the course of the etching (the maximum of the band from 830 to 620 nm), which is demonstrated in Figs. 4 and 6.

We note that the PL intensity varies during the treatment in HF vapors nonmonotonously: it increases as a result of a short-term etching, attains a maximum value at the treatment of specimens during 10 min, and then begins to decrease. Since O_3SiH complexes can be localized only in the silicon-oxygen phase which surrounds a Si nanoinclusion and cannot be assigned to the surface of a nanoinclusion or a transient nanoinclusion – oxide layer (this will occur if the complex has at least a single bond Si–Si), we may conclude that the passivation of broken bonds of silicon on the surface of a nanoinclusion by hydrogen has a low probability. The passivation of such bonds by oxygen during the formation of an oxide layer on the nanoinclusion surface, as well as by fluorine, is more probable. In the last case, we observe the formation of complexes of the Si_3–Si–F type on the surface of a nanoinclusion. The presence of such complexes in etched specimens is indicated by IR-spectroscopy.

Thus, the observed changes in the IR and PL spectra as a result of the treatment of porous nanocomposite Si/SiO_x films in HF vapors can be explained as follows. During the etching in vapor, gas-like molecules HF pen-

etrate easily into a porous nanocomposite Si/SiO_x film. Then the selective dissolution of SiO_2 from the surfaces of structural columns starts by the reaction



$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Tetrafluorosilicon (SiF_4) can be released, as a gas-like substance, through pores of a structure, and the broken bonds of silicon on the surface of nc-Si are passivated by oxygen. The oxidation of silicon nanoinclusions begins, first of all, on external monolayers of nano-sized silicon, which decreases the initial size of a nanoparticle and is revealed, according to the quantum-size effect, in a short-wave shift of PL spectra of specimens after their treatment. The more the etching duration, the less the size of a Si-nucleus. The mechanism of the decrease in sizes of nc-Si due to the treatment by HF is analogous to the effect of the aging of nanosilicon-containing specimens in air [25]. They differ from each other only by the rates.

The decrease in the size of Si nanoinclusions and the passivation of the surface of Si nanoinclusions at the formation of new chemical bonds of the Si-O and Si-F types occur simultaneously, which corresponds to an increase in the emission intensity with decrease in the size of nc-Si. The passivation of centers of nonradiative recombination in porous nanocomposite specimens Si/SiO_x due to the treatment by HF vapors is also supported by the results of our studies of ESR spectra [26].

If the etching duration exceeds the optimum one (t >10 min), the PL intensity begins to gradually decrease due to a diminution of the amount of nanosilicon in specimens of the film. Thus, the basic changes of luminescence properties of nanocomposite systems Si/SiO_x after their treatment by HF vapors can be described by the process of modification of an imperfect state of the nanoinclusion-Si–SiO_x interface.

4. Conclusions

We studied the influence of the etching of the oxide matrix by HF vapors on IR-spectra and the photoluminescence spectra of porous nanocomposite Si/SiO_x structures produced with the help of the oblique deposition and the high-temperature annealing in vacuum. We have shown that the treatment in HF vapors causes a significant decrease in the volume of a film and the partial additional oxidation of its surface, as well as the formation of complexes O_3SiH and O_2SiF_2 in the film. On the surface of silicon nanoinclusions, complexes Si_3SiF arise. Using the selective etching, we managed to obtain a significant shift (up to 210 nm) of the emission maximum from the IR range to the visible one of the spectrum, as well as a significant (more than 2 orders) increase in the luminescence intensity. These effects can be explained by the process of modification of a structural defective state of the nanoinclusion-Si–SiO_x interface as a result of the action of the etcher on a porous film. The light emission intensity increases due to the passivation of broken bonds of silicon on the surface of Si nanoinclusions by atoms of oxygen and fluorine. The oxidation of the surface of silicon nanoinclusions decreases their size, which is revealed in a short-wave shift of PL spectra.

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ВПЛИВ ОБРОБКИ У ПАРАХ HF НА СТРУКТУРУ ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ ПОРУВАТИХ Si/SiO_x НАНОКОМПОЗИТІВ

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Р е з ю м е

Методами ІЧ-спектроскопії та фотолюмінесценції досліджено вплив травлення парами HF оксидної матриці поруватих нанокомпозитних Si/SiO_x структур. Структури отримували термічним осадженням монооксиду кремнію у вакуумі під кутом 60° на *c*-Si підкладці з подальшим відпалом при 975 °C. Показано, що обробка у парах HF приводить до значного зменшення об'єму плівки і часткового доокислення її поверхні, а також до появи у плівці комплексів O_3SiH та O_2SiF_2. На поверхні нановключень кремнію з'являються комплекси Si_3SiF. Одночасно спостерігають суттєвий (до 210 нм) зсув максимуму випромінювання з інфрачервоного у видимий діапазон спектра, а також значне (до 200 разів) збільшення інтенсивності люмінесценції. Ці ефекти можна пояснити процесом модифікування структурно-домішкового стану межі поділу нановключення $Si–SiO_x$ в результаті дії травника́ на поровату плівку. Інтенсивність світловипромінювання зростає внаслідок пасивації обірваних зв'язків кремнію на межі поділу нановключення $Si–SiO_x$ атомами кисню та атомами фтору. Оксидування поверхні кремнієвих нановключень зменшує їх розмір, що проявляється у короткохвильовому зсуві спектрів ФЛ.