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Photoluminescence of Por-Si with High-ordered Mosaic Structure Received at Long Anodic Etching p-Si (100) in the Electrolyte with an Internal Current Source

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ABSTRACT

Photoluminescence spectra and nature of light-emitting centers of a porous silicon (por-Si) samples are given. The por-Si samples had high-ordered mosaic structure, which was received under long anodic etching p-Si(100) in electrolyte with an internal current source. The photoluminescence spectra were monitored at room temperature before and after annealing in air and vacuum. Comparative analysis of photoluminescence spectra of the por-Si samples annealed at different temperatures in air and vacuum shows that the thermal annealing conditions has significant effect on the intensity and spectral content of the photoluminescence spectra. The nature of the luminescence emission centers at different temperatures and annealing conditions was discussed.

Keywords: Photoluminescence Spectra; Thermal Annealing; Emitting Centershydrides; Oxides; Mosaic Structure; Nanocrystallite; Por-Si

1. Introduction

Today, a large number of works dedicated to the study of photoluminescence (PL) properties of por-Si, promising for practical applications, such as LEDs. The por-Si includes silicon nanocrystallites (Si-NCs) in the form of nanowires on the surface layer of monocrystalline silicon with different phases of crystalline c-Si and amorphous a-Si, covered with oxides (SiO_y) and hydrides (SiH_x). The nature of light-emitting centers (LEC) PL is still not a fully established and different models are offered for its explanation [1]. One of the earliest and the most widely used models is quantum model PL in which the luminescence is determined by the recombination of excitons in the Si-NCs. Another model suggests that the luminescence related to hydride (Si-Hx) bonds on the surface of Si-NCs por-Si. There is also a model of the PL related to the presence of defect centers in oxides (SiO_y) at the interface of Si-NCs por-Si/SiO_y. The most widely accepted model for explaining the maximum intensity of PL at λ_{max} = 640 nm associated with the defective levels of complexes hydrides and oxides on the surface of nanocrystallites (NCs), such as SiH_x or SiO_y (x, y = 1-4). Maximum PL intensity at λ_{max} = 440 nm related to radiative recombination of excitons in Si-NCs por Si [2].

In our report, it considers the nature of the PL and light- emitting centers in por-Si with high-ordered mosaic structure (MS), received at long anodic etching p-Si(100) in electrolyte with an internal current source [3].

2. Experimental Results and Discussion

The PhL spectra of samples with MS of por-Si received at room temperature before and after annealing on air and in vacuum are presented. Samples Si (B), ρ = 0.01 $\Omega \cdot$cm and with plane of crystallographic orientation (100), were carried out etching in the electrolyte HF (49%): H_2O_2 (40 %) = 1:1. Ohmic *In*-contacts were created on the back side of the samples by annealing at 300℃ during 30 min. Anode was p-Si, cathode - Ni. The densities of anodic current were j_a = 3.0 mA/cm^2. The porous surfaces of silicon were researched by the scanning electron (JSM-6490LA) and atomic force (JSPM5200) microscopes.

PhL excitation was carried out He-Cd laser at a wavelength of λ_{exc} = 325 nm with output power 15 mW, focused on the sample surface by patch with diameter of 1.0 mm. Thermal annealing of freshly prepared samples of por-Si was carried out both on air and under controlled conditions of a vacuum 10^{-4} Torr (sputtering unit ARC 2000) in the temperature range 50℃ - 500℃ at steps of 50°. It was found, that the PhL observed at room temperature as a red-orange glow in the place of incidence of

the exciting laser radiation on the islets of NCs por-Si, while the silicon ledges and cell- the free sites from islets no show light-emitting properties.

Islets of NCs por-Si is an ensemble of clusters oxi- dized Si-NCs with size about 10 nm - 20 nm [4], and free cell and ledges are the pure silicon [5]. Comparative analysis of the PhL spectra of samples of por-Si, annealed on air and in vacuum shows a significant the annealing effect on parameters PhL. It is seen, that the PhL spectra, received under these conditions have similarities and im- portant differences. The PhL spectra of freshly prepared samples of por-Si, received at room temperature, repre- sent broad band and have two characteristic regions of maximum intensity of the light emitting at wavelengths of $\lambda_{max} = 640$ nm and $\lambda_{max} = 440$ nm (**Figure 1**).

The dominantly long-wavelength maximum of the PhL spectrum $\lambda_{max} =$ at 640 nm usually associated with the recombination of charge carriers at the defect centers of the surface of hydrides and oxides coatings of Si-NCs por-Si, while the short-wave maximum of the PL at $\lambda_{max} = 440$ nm with recombination of excitons in the itself of Si-NCs [2].

In our case, in the long-wave part of spectra, received both in air and vacuum, on the short-wave their wings in the region of $\lambda = 600$ nm, the inflection is observed. This indicates on the presence of two different emitting centers. The superposition of their spectra and gives this inflection. It can be assumed, that the emitting center responsible for the inflection in the $\lambda = 600$ nm, due to the presence of containing carbon-silicon complexes [6]. The presence of carbon in the samples of the por-Si may be due to the adsorption of carbon-containing molecules from the air, which is confirmed by our results of elemental analysis [5]. The nature of short-wave part of the PhL spectrum at $\lambda_{max} = 440$ nm coincides with published data [2].

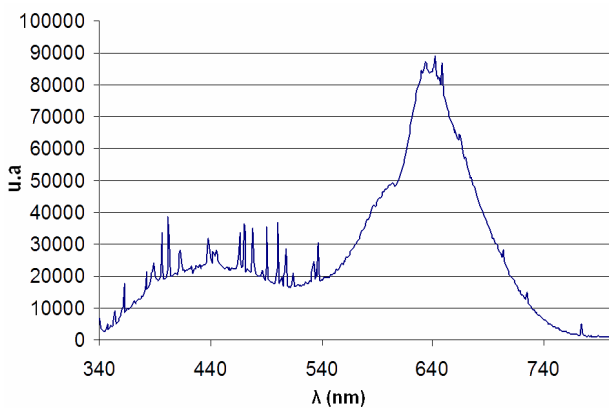For a more complete understanding of the nature emitting centers the PhL was performed thermal annealing of

ceived in electrolyte HF(49%):H_2O_2 (40%), $t_{etch.}$=4 h.
the samples por-Si on air and in vacuum, when at annealing gradually removes the adsorbate, which is a reaction product of etching and adsorption from the environment, and at this possibly transformation of their structures [6].

Thermal annealing of the samples freshly etching por-Si showed, that the maximum PhL intensity at a wavelength of $\lambda_{max} = 640$ nm observed at $100℃$ annealing both on air and in vacuum (**Figures 2**, **3**). The increase intensity of the PhL at $T_{ann} = 100℃$, is usually, attributed to desorption of water molecules in this temperature range [7,8].

In both cases are observed a broadening of the long-wavelength wing of the PhL spectrum by shifting the wavelength of maximum emitting and the significant growth of the PhL signal in the highly-energy part of the spectrum. While its the short-wavelength wing of the PhL spectrum is practically unchanged.

This experimental fact differs from the published results, when there is a broadening of the highly-energetic wing the PL spectrum with shift of the maximum intensity to highly-energetic region [9], or broadening of the low-energy wing of the PL spectrum with shift of the maximum intensity, but at this case is observed the decrease in PL intensity [10].
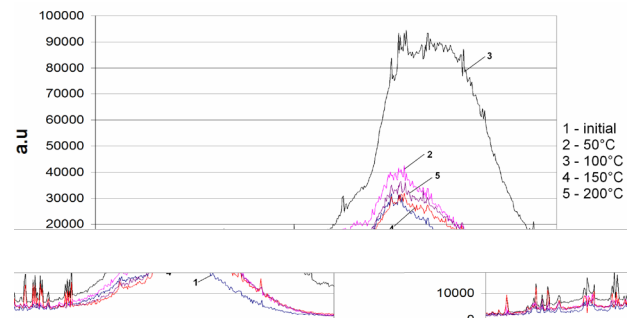

Figure 2. The PL spectrum as a function of annealing temperature sample in vacuum 10^{-4} Torr.

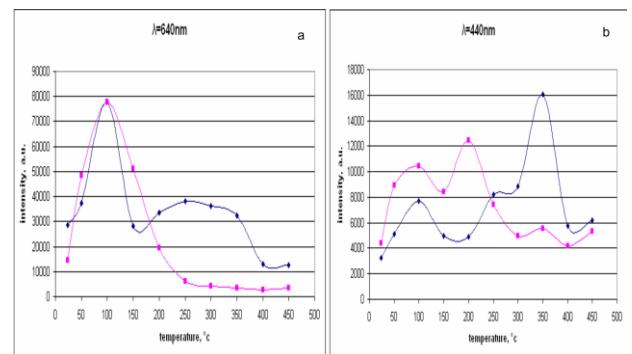**Figure 1. The PhL spectrum of the samples por-Si, the re-**

Figure 3. Dependence of the maximum intensity of the PL spectrum at $\lambda_{max} = 640$ nm (a) and $\lambda_{max} = 440$ nm (b) as a function of annealing temperature (■ -on the air ♦ - in

vacuum 10^{-4} Torr).

Typically, according to quantum-size model the PL maximum shifts to high-energy side as a result of reducing the sizes of Si-NCs. The broadening of the low-energy wing of the PhL spectrum are explained increasing the sizes Si-NCs at additional processes of hydrogenation and oxidation the surface Si-NCs at or after the desorption of water. At the same time possible reconstruction of structure of hydride SiN_y and oxide SiO_x (x, y = 1-3) complexes on the surface of Si-NCs in more complex structures of various sizes. Low-energy maximum of the PhL spectrum of our samples is determined by irradiative recombination in non-quantum-size NCs por-Si [11], due to fluctuations potential in the highly developed surface of por-Si, leading to a localization of charge carriers. In our case, a significant increase in the intensity of the low- energy maximum PL by compared with the high-energy maximum of intensity of PhL spectrum is determined by the size of Si-NCs por-Si, which are mostly of the order of 10 nm - 20 nm. It should be noted the following interesting experimental result, when a small increase in vacuum of temperature annealing to $T_{ann.} = 150℃$, only on 50°, maximum intensity reduces to the initial state and returns the original form of the long-wavelength part of the spectrum (**Figure 3**).

Recovery of intensity and line shape of the PhL maximum at $\lambda_{max} = 640$ nm for small change in the annealing temperature suggests, that the irreversibly structural changes in the volume of Si-NCs does not occur, but only changes the surface structure. That is, at this annealing temperature take place the reconstruction of the surface coating without significant changes in their chemical and structural state of the surface of Si-NCs por-Si. This is confirmed by the fact that the decrease in PL intensity occurs without a significant change in the shape of the spectrum. All this only shows the transformation of chemical bonding and structure the surface hydrides and oxide complexes. That is, as a result of desorption of water molecules from the surface of NCs por-Si take place the transformation of complex systems at chemisorptions of H and O, and thus decreases the PhL intensity due to shielding of the emitting centers with these complexes. In the case of annealing at $T_{ann}= 150℃$ on air maximum intensity decreases to lesser extent (**Figure 3(a)**) than during annealing in a vacuum, retaining the original shape of the spectrum before annealing. The fact, that at annealing on air the maximum intensity of the PhL spectrum is reduced to lesser extent than in the case of annealing in a vacuum, can be explained the possible formation of more complex systems, involving oxides. It is possible, that they are either give the weakly the shielding the emitting centers compared with complexes, formed at vacuum, or in these complexes are formed more defective emitting centers. **Figure 4(a)** shows, that

a further increases in air the temperature annealing to $T_{ann.} = 250℃$ the PhL intensity monotonically decreases, and in range $T_{ann.} = 300℃ - 450℃$, its intensity becomes minimum and practically almost constant, and disappears at $T_{ann.}= 500℃$. This well-known experimental fact that the decrease and disappearance of the PhL signal upon annealing in the range $T_{ann.} = 250℃ - 500℃$ due to the formation of surface stable oxide layer, which can either to shield emitting centers [6] or to replace hydrides on oxides [7]. In addition, the PhL intensity can be reduced, as we believe, due to annealing emitting defects centers the surface complexes.

It is interesting to note, that the intensity of the PhL signal samples por-Si, annealed at $T_{ann}= 250℃ - 350℃$ in a vacuum, more higher (8 times), than signal PhL intensity of the samples por-Si, annealed at the same temperatures on air.

In samples annealed in a vacuum, the high PhL intensity continues observed up to $T_{ann.}= 400℃$, in contrast to the samples annealed in air. Sufficiently intense PhL signal, observed during annealing in vacuum at $T_{ann.} = 250℃ - 350℃$ is explained the presence of hydride bonds of Si_xH_y, which were formed during etching of
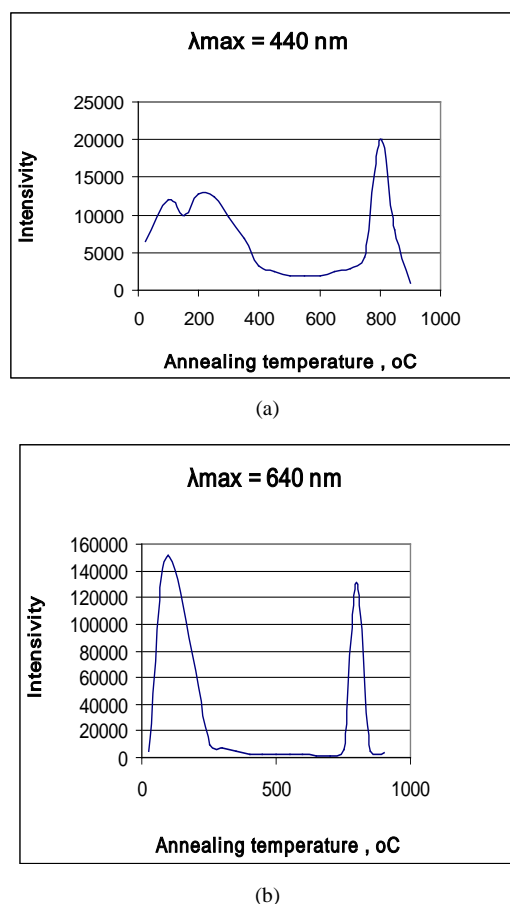

(a)

(b)

Figure 4. Dependence of the maximum intensity of the PL

spectrum at λ_{max} = 440 nm (a) and λ_{max} = 640 nm (b) as a function of annealing temperature on the air.

crystalline silicon and is dominated by these annealing conditions [6]. The sharp drop in PhL intensity at $T_{ann.}$ above 350℃ is due to the loss of the hydrogen coverage [12] as a result of dehydration of the surface emitting NCs centers and growth the concentration of the centers of non-emit- ting recombination due to the formation of dangling bonds in silicon [13].

Previously, according to IR Fourier spectroscopy has been installed complete correlation between the change in signal PhL intensity and absorption intensity in all types of bonds SiH [14]. About this is also evidenced by recent results of the study the influence of aging on the PhL of por-Si, obtained by ultrasoft x-ray emission spectroscopy USXES [1,15], which shows the influence of phase composition of samples of the por-Si on the intensity and position of the PhL peak. In fresh samples of por-Si dominated the amorphous hydrogenated phase of silicon a-Si:H (48%) and crystalline phase c-Si (42%), and only 10% are oxide phases SiO_x + SiO_2.

Thus, the long-wave PhL spectrum at λ_{max} = 640 nm is changed of due to formation the hydride complexes $(Si_xH_y)_n$, in the process of porous formation.

For the PhL signal in the short-wave range with λ_{max} = 440 nm (**Figure 3(b)**) in samples annealed in air, there are two maxima at $T_{ann.}$= 100℃, and more intense at $T_{ann.}$= 200℃. Upon further annealing them on air, there is a monotonic decrease of PhL signal with a small splash at $T_{ann.}$ = 350℃.

In samples annealed in a vacuum, apart from the peak intensity of the PhL signal at Tann = 100℃ has increase in signal in the region 200℃ - 250℃, with access on the plateau at $T_{ann.}$ = 250℃ - 300℃. At $T_{ann.}$ = 350℃ has a sharp increase in the PhL signal, which at further at $T_{ann.}$= 400℃ rapidly decreases and disappears at 500℃.

This ambiguous behavior of photoluminescent properties of por-Si during annealing in air and vacuum in the short-wave side of the PhL spectrum can be explained by the manifestation of emitting centers in Si-NCs due to the change of the phase and elemental composition of a multicomponent, complex structure of the surface of NCs por-Si. The increase the PhL signal at 100℃ both in air and in vacuum due to the removal of water, which screened emitting NCs centers. There is a second maximum PhL at $T_{ann.}$= 200℃ in air, which is more intense, than the first at 100℃. This maximum may be due to the formation of siloxane compounds during annealing in air [8]. At this temperature annealing in vacuum formation of siloxane complexes does not occur, therefore the PhL signal don't observed.

Decreasing the PhL signal at 200℃ and above on air take place due to oxidation of the surface of Si-NCs. This may be as a result of the formation of stable oxides at

removing hydrogen from the complexes of the type $Si_6O_3H_6$.

The growth of the signal PhL intensity at $T_{ann.}$ above 200℃ in vacuum is explained due to the formation of different hydride complexes $(Si_yH_x)_n$. At $T_{ann.}$ above 350 ℃ take place dehydrogenation surface emitting centers Si-NCs and as is observed a sharp decrease of PhL intensity. The observe small increase of the intensity of the PhL signal at $T_{ann.}$= 350℃ on air has a similar nature, as for por-Si samples annealed in vacuum.

The intensity of the long-wave part of the PhL spectrum for 1 hour exposure of laser radiation decreases more strongly (8 times), than in the short-wave part (2 times). A further increase of exposure time practically does not change the intensity of the PhL spectra.

The change of PhL intensity is reversible, after stop of illumination is observed the restoration of the original PhL intensity in during several hours. Such a reversible change signal PhL can be explained by changes in the dielectric constant of the medium surrounding the Si-NCs [6] through of photo-stimulated reactions on the surface of por-Si at illumination [8]. At this forms of dangling bonds and as a consequence non-emitting recombination centers. At exposed on air take place reversible "healing" of dangling bonds in the process of natural oxidation of the surface of NCs por-Si.

Finally, the high-temperature annealing air at T = 800 ℃ leads to the appearance the PL signal (**Figure 4 (a), (b)**).

This fact we associate with the internal of oxidized of silicon at these annealing temperatures on the air, when the formation of light-emitting centers in the form of oxides of silicon. Such is not observed during annealing in a vacuum.

3. Conclusions

Thus, 1) maximum intensity of PhL spectra of por-Si samples at $T_{ann.}$= 100℃ on air and in vacuum is changed of due to thermal desorption of H_2O molecules from the surface of light-emitting centers in the por-Si; 2) long-wave part of the PhL spectrum of samples por-Si in the field λ_{max} = 640 nm for freshly prepared samples is due to emitting recombination of excitons in non-quan-tum-size crystallites por-Si dimensions, mainly of 10 nm - 20 nm and surface hydride complexes of the type $(Si_xN_y)_n$, formed in the process a pore formation; 3) low intensity short-wave part of the PhL spectrum of for freshly prepared samples in the region λ_{max} = 440 nm due to of quantum-sized crystallites (1 nm to 1.5 nm); 4) thermal variation of the maxima of the intensity of the short and long-wave part of the PhL spectrum is due to the transformation of hydride SiH-bonds in the porous surface during annealing in vacuum and on air in the temperature range $T_{ann.}$ = 200℃ - 400℃; 5) degradation the emitting

centers at $T_{ann.} > 400\,℃$ and complete absence of PhL at $T_{ann.} > 500\,℃$ are observed due to the delete of hydride SiH-bonds on the porous surface; 6) long excitation of PL leads to heating that transforms of hydride complexes. This fact confirms, that the light emitting centers are formed due to hydride coverages of surface NCs por-Si; 7) annealing at $T_{ann} = 800\,℃$ of por-Si on air leads to the formation of light-emitting centers in the form of oxides of silicon.

4. Acknowledgements

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