Porous silicon as a low dimensional and optical material

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Abstract. The considerable and controllable changes in electronic structure and refractive index of porous silicon fabricated by electrochemical anodization make it become a promising material for photonics in comparison with bulk silicon. As the study of PS in terms of a low-dimensional material, we reviewed the effect of the surface passivation of silicon nanocrystals on photoluminescence spectra of such zero-dimensional crystals. In terms of an optical material, we show the fabrication method and optical properties of planar waveguide as well as active waveguide operated in the range of 1.54 µm wavelengths. We have also investigated the effect of energy transfer from silicon nanocrystals to erbium ions based on erbium-doped porous silicon waveguide.

Keyword: Porous silicon, electrochemical, nanocrystals.

1. Introduction

Since 1990 when Canham reported on the efficient visible photoluminescence (PL) from porous silicon (PS) [1] this material has attracted an increasing interest for research as well as applications [2]. The considerable and controllable changes in electronic structure and refractive index of PS fabricated by electrochemical anodization make it become a promising material for photonics in comparison with bulk silicon. In the structure, PS consists of many micropores and silicon residuals with the size and width of the order of a few nm. The exciton Bohr radius in Si is around 4.3 nm, so that quantum confinement can occur and change in electronic structure of those silicon nanocrystals [3]. On the other hand, because the value of porosity (the fraction of Si removed from the substrate) is directly linked to the effective index of refraction of the PS layer, this layer appears as an effective medium, whose refractive index has a tunable value between the index of refraction of bulk Si and that of the air (pores) [2]. The considerable and controllable changes in electronic structure and refractive index of PS as compared to bulk Si make it fascinating in terms of both a low-dimensional material and an optical one.

In the initial work [1], Canham proposed that the upshift of the luminescence spectrum into the visible was due to quantum confinement in the silicon crystalline wire structure and hydride passivation of the Si wire was the reason for the high efficiency of the observed PL. For a no-long time after that, spectroscopic studies, particularly those of the polarization of the PL [4, 5] and of features observed under conditions of resonant excitation [6], have provided strong positive proof of the quantum confinement model. However, there were a lot of spectroscopic phenomena that can not be explained in the frame of the simple quantum confinement model. In this embarrassing situation,
numerous models have been proposed as alternative explanations of the PL from PS such as hydrogenated amorphous silicon, surface hydrides, defects, molecules, surface states [3]. It is well known that in PS the surface to volume ratio is very large, so the surface effects are expected to play an important role in the material properties, especially optical ones [7]. Because the Si atoms in Si nanocrystals are either at the surface or a few lattice sites away, the arrangement of interfacial atomic bonds, i.e. the passivation with Si-H or Si-O bonds, strongly affects the energy distribution of electronic states [8]. In this paper, we present effects of ageing on the spectral, intensity and lifetime of PL from PS. Our results show that the effect of the surface passivation on the re-distribution of electronic states and the luminescence efficiency is dependent on the size of nanocrystals in PS.

As study of PS in terms of a low-dimensional material, we focus attentions on strong emission properties and employ PS as materials for light sources, i.e. light emitting diodes and lasers operated in visible region. Concentration on controllable changes in refractive index of PS, we would like to use PS as materials for filters, optical planar waveguides and amplifier waveguides. In the paper, we also present the fabrication method and properties of optical planar and amplifier waveguides operated in the range of 1.54 µm wavelength. An advance of amplifier waveguides based on Er-doped PS is effect of efficient energy transfer from electron-hole pairs generated in the Si nanocrystals to their near erbium ions, which radiatively decay by emitting photon at 1.54 µm. The effective Er excitation cross-section in Er-doped PS is more than two orders of magnitude higher with respect to the Er resonant absorption of a photon [9], so that the pump efficiency in amplifier Er-doped PS waveguides can be very high. The effect of energy transfer has also been explored in elaborated Er-doped PS waveguides. With the before-mentioned aim this paper consists of sections as following: 2- PS as a low-dimension material, 3- PS as an optical material, and 4- conclusions.

2. Porous silicon as a low-dimension material

In the first of this section we present the affect of surface states on the PL properties of PS based on the ageing process in the air. In the last, we would like to show the reason for the intense and stable luminescence in the blue region which has been of interest in recent studies [10].

![Image](image.png)

**Figure 1.** PL spectra of the as-prepared samples and after exposure to air for 1-month; samples, denoted as 1, 2 and 3, were prepared by the anodical etching in 20%, 13%, and 10% HF solution, respectively. (a) sample 1, (b) sample 2 and (c) sample 3 [10].

Previous studies on the interaction of oxygen in the air on the as-prepared PS [8] show that i) the samples as-prepared were well passivated by hydrogen and free of oxygen, ii) after exposure to air the samples were gradually passivated by oxygen and the red-shift of PL spectral occurred as exposure samples to air and was nearly completed after ageing of 24 h. They suggest that the ageing process can be divided into periods: the first one in which the transition of the luminescence mechanism occurs after exposing samples to air for a short time and the second one in which non-radiative centre concentration is changed by oxygen passivation [11].
In order to reveal the dependent of surface passivation effect on the size of Si nanocrystals a series of PS samples, denoted as 1, 2 and 3, were prepared by the anodical etching in 20%, 13% and 10% HF solution, respectively. As seen in figure 1, the PL peaks of the as-prepared samples 1, 2 and 3 have energy of 1.73, 1.84 and 2.00 eV, respectively. It is related with a decrease of particle size in the considered samples. The figure also reveals that the ageing produces a pronounced increase in PL intensity from sample 1 and only a small increase for samples 2 and 3. As seen in figure 2, the decay rate of the as-prepared samples (the curves 1a, 2a and 3a) shows that concentration of non-radiative centers in the sample 1 is higher than those in samples 2 and 3. The pronounced increase in intensity (in figure 1) as well as the pronounced decrease in decay rate (in figure 2) of sample 1 could be caused by the oxygen passivation of non-radiative defects. In the samples 2 and 3 containing smaller particles, the initial passivation degree is higher, therefore the ageing is expected to induce a small change both in intensity and decay rate. The comparison of data from curves 2a and 2c in figure 2 reveals that the modification of emission mechanism has no effect on the decay rate as well as its energy dependence τ⁻¹(E). This result seems to indicate that the replacement of Si-bond by Si-O one acting as a radiative center has no effect on the lifetime.

![Figure 2](image1.png)
**Figure 2.** Evolution of decay rate as a function of emission energy from samples after preparation, curves 1a, 2a, 3a and after exposure to air for 1-month, curves 1b, 2b. Curve 2c corresponds to sample 2 for 24 h [10].

![Figure 3](image2.png)
**Figure 3.** Evolution of PL spectral measured at the end of excitative pulse from a PS sample after different exposure time (1): as-prepared, (2): after 26, 72 and 94 h of exposure to air, respectively, (4im): corresponding to sample exposed to air for 94 h. and then immersed in 5% HF: ethanol solution for 10 sec [12].

From figures 1 and 2 the relation between the size of particles, intensity and decay rate during ageing was received. In the sample containing larger nanocrystals, the change of intensity and decay rate, i.e. the luminescence lifetime, are much larger during ageing.

Figure 3 shows the evolution of PL spectra, measured at the end of an excitative pulse after different exposure time. The figure reveals that the blue zone with the PL emission peaked at 470 nm is only observed after 72 hours of exposure to air. Furthermore, the figure also reveals that the PL intensity increases by increasing the air exposure time. These observations are different as compared to those reported in reference [8] in which the intensity of blue emission from the as-prepared sample containing the small Si particles was shown to decrease as the exposure time increased. This result indicates that blue-light emission observed in the present work does not arise from very small nanocrystals. Curve 4im shows the PL spectrum of a sample, which has exposed to air for 94 hours and then immersed in HF: ethanol solution. Comparing curves 4 and 4im, one can state that the blue zone in the PL spectrum, observed for the sample after 94 hours of exposure to air, is completely quenched. This quenching clearly relates to the fact that the silicon oxide layers in the exposed sample
have been removed. The above results indicate that the intense and stable emission in the blue zone of the PL spectra, which observed in considered samples, relates to defects in silicon oxide layers.

3. Porous silicon as an optical material

In this section, before presentation of the fabrication method and properties of optical planar and amplifier waveguides we would like to show the ways of producing PS multilayer which is the base of elaboration of those waveguides. In the last, effect of energy transfer in prepared samples is shown.

Two main ways of producing PS multilayer have been proposed up to now [2]: by periodically varying the etching parameters, such as for the current density or the light power on the surface of Si under etch, or by using periodically doped substrates and maintaining constant the various etching parameters. In the following we will discuss the first approach, because it is more easily accomplished and it has been the one employed by us. This approach is based onto the following statements:

- the etching process is self-limited (once a porous layer is formed, the electro-chemical etching of this layer stops);
- the etching occurs mainly in correspondence to the pore tips;
- the porosity depends only on the current density once the other etching parameters are kept fixed;
- the refractive index of PS, n, depends on its porosity;

Hence, by varying the current density during the etch process, it is possible to vary the porosity in the etching direction only at the etch front. In this way, the current versus time profile is transferred in the porosity versus depth profile, i.e. n versus depth profile.

Our preparation process for an optical planar waveguide consists of 2 steps: making a PS film containing a core layer and a cladded one and stabilizing the structure of the PS film by thermal annealing at high temperature. In the fabrication of an optical amplifier waveguide, a step of deposition of Er ion into the PS film is added before thermal annealing. The treatment in high temperatures can cause an optical activation of Er ions in PS.

![Figure 4. Core-cladding structure of PS film on Si-substrate of a planar waveguide layer.](image)

The PS films were formed by electrochemical etching of 1Ωcm p-type Si wafers in 30%HF: ethanol solution. The top core layer has been fabricated by applying a 15 mA/cm² for 7 min. The cladding has been formed in the same way, with a 65 mA/cm² current density for 3 min. These conditions allow receiving a porosity of about 60% and 65%, corresponding, to the core and cladding. To deposit Er ions into the PS layers, the film was immersed in a 0.2 M ErCl₃ solution and the negative bias, relative to a platinum electrode, was applied to the sample at a constant current density in the range from 175 μA/cm² to 450 μA/cm² for 5 min. For optical activation of Er ions distributed in pores of PS layer, the sample was annealed at 400°C for 2 h, and then at 800°C for 15 min. in dry oxygen.

A cross section of the PS film was characterized by using a Scanning Electron Microscopy (SEM) measurement as presented in figure 4. Based on the different contrast between the core and the cladding due to the difference in porosities, it is observed that the film consisted of two layers in
which the core layer thickness is about 4.5 μm, and the cladding about 7 μm. These data consisted with the layer thickness received from the prism-coupling method.

Figure 5 shows the SEM image of surface of the core and cladding before and after the period of thermal annealing. As seen from figures 5a and 5c, the difference in density of the black area presented the pores in the PS layer shows that the porosity in the core layer is lower than that in the cladding. From this figure we also observed the differences in density of the black area and in the contrast between the black area and the while one from the PS layers before (figures 5a and 5c) and after (figures 5b and 5d) the thermal treatment. Those differences appear that the treatment can cause decrease in the size of pores and the porosity of PS layers. The prepared PS layers have been densed and therefore optical properties of the waveguides would be stabilized.

Figure 6 shows the m-line received from the prism-coupling measurement in the prepared samples. As seen in figure 6a, the optical waveguide effect did not occur in the sample containing only a core layer. However, the m-line in figure 6b from the sample having the core-cladding structure showed an existence of the coupling angles at which the waveguide effect appeared. Base on the measured coupling angles, the effective refractive indices of 1.45 and 1.42, respectively, from the core and the cladding layer have been determined. The prepared optical waveguide with a refractive index contract up to 0.03 is suitable in optical integrated devices.

![SEM image of surface of the core and cladding before and after thermal annealing](image)

**Figure 5.** SEM image of surface of the core (c, d) and a PS layer, which was prepared in the same etching parameters for the cladding (a, b) before (a, c) and after (b, d) thermal annealing in order to estimate their porosities.

![M-line from prism-coupling measurement](image)

**Figure 6.** The m-line from the sample having the single layer structure (a) and the core-cladding structure (b) in order to determine the waveguide modes and effective refractive index of each layer.

As above mentioned, Er ions need to incorporate into the core layer during the fabrication process of the amplifier waveguides. In our method, the Er-ion concentration, which doped into PS, can be
controlled by Er concentration in ErCl\textsubscript{3} solution or drift current density in electrochemical cell. For the purpose of obtaining high-concentration Er-doped SRO materials (more than 0.1 at.% of Er) without Er-clusters, that will be good candidate for planar-waveguide amplifier, we have carried out very careful study of the distribution of Er-ions along the depth of the prepared PS layers. Figure 7 shows the Er concentration profile as a function of the waveguide depth that has been characterized by EDX method with the SEM technique. The Er-ion concentration was increased from 0.11 at.% from top-surface to 0.2 at.% at the depth of 3.5 \( \mu \text{m} \) from the top-surface. But the Er-ion concentration became decreased with the depth inside the samples.

**Figure 7.** Er concentration profile as a function of the waveguide depth.

Figure 8 presents the luminescence spectra at 1550 nm-region of the samples with different drift currents from 0.17 to 0.45 mA.cm\textsuperscript{-2} under excitation of 976 nm-laser beam. The 1550 nm-luminescence intensity of all kind of samples has been increased with increasing drift current density from 0.17 to 0.25 mA.cm\textsuperscript{-2}, but when the drift current density is more than 0.25 mA.cm\textsuperscript{-2} the luminescence would be slightly decreased with increasing the drift current.

**Figure 8.** Luminescence spectra from samples 1, 2 and 3 under drift current density of 0.17, 0.25 and 0.45 mA, respectively.

In general, the intensity of luminescence emission at 1550 nm-region would be increased with increasing the concentration of Er-ion in PS layer. However, as the Er-ions concentration has reached the certain value, the luminescence intensity at 1550 nm-region would be decreased by the quenching effect from Er-ion clusters [13].

Figure 9 demonstrates the photoluminescence intensity at 1534 nm on the power of the excitation laser at wavelengths of 488 nm and 976 nm.

**Figure 9.** Dependence of luminescence intensity at 1534 nm on the power of the excitation laser at wavelengths of 488 nm and 976 nm.
pump at 976 nm only causes a direct excitation of Er ions (from $^4I_{15/2}$ to $^4I_{13/2}$ level), whereas the pump at 488 nm causes both a direct excitation of Er ions (from $^4I_{15/2}$ to $^4F_{7/2}$ level) and an indirect one related to the energy transfers from Si-nc to Er ions. Because the effective Er excitation cross-section in Er-doped PS is more than two orders of magnitude higher with respect to the Er resonant absorption of a photon, so that the pump at 976 nm causes a linear dependence of intensity on excited power [14] and the pump at 488 nm causes the non-linear one as seen in the figure.

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