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Influence of current density, anodization time, and illumination on the thickness of porous silicon in wafers with the built-in *p–n* junction and its photoluminescence

D. T. Yan [1] ✉, N. G. Galkin [2], K. N. Galkin [2], A. V. Nepomnyashchiy [2]

[1] Far Eastern State Transport University, Khabarovsk, Russia;
[2] Institute of Automation and Control Processes FEB RAS, Vladivostok, Russia
✉ dmitry_yan@mail.ru

Abstract: The formation of a porous silicon (por-Si) layer in a thin *p*-type layer epitaxially grown on *n*-type silicon, at two anodizing current densities and different anodizing times is studied and a comparison is made of transverse cleavages, surface morphology, reflection spectra, and photoluminescence spectra. The minimum duration of anodizing (15 and 10 minutes) at current densities of 10 mA/cm^2 and 20 mA/cm^2, at which a single-layer PS structure is formed, is established. With an increase in the anodization time, regardless of the current density, a two-layer structure is formed with an internal tree-like porous silicon layer, whose contribution to photoluminescence is minimal, and the reflection coefficient drops strongly due to irretrievable losses in the porous tree-like layer.

Keywords: silicon, built-in *p*—*n* junction, current density, anodization time, illumination, porosity

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Материалы конференции
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Влияние плотности тока, времени анодирования и освещения на толщину пористого кремния в пластинах со встроенным *p–n* переходом и его фотолюминесценцию

Д. Т. Ян [1] ✉, Н. Г. Галкин [2], К. Н. Галкин [2], А. В. Непомнящий [2]

[1] Дальневосточный государственный университет путей сообщения, г. Хабаровск, Россия;
[2] Институт автоматики и процессов управления ДВО РАН, г. Владивосток, Россия
✉ dmitry_yan@mail.ru

Аннотация. Исследовано формирование слоя пористого кремния (ПК) в тонком слое *p*-типа, эпитаксиально выращенном на кремнии *n*-типа, при двух плотностях тока анодирования и разном времени анодирования, и проведено сравнение поперечных сколов, морфологии поверхности, спектров отражения, и спектры фотолюминесценции. Установлена минимальная продолжительность анодирования (15 и 10 минут) при плотностях тока 10 мА/см^2 и 20 мА/см^2, при которых формируется однослойная структура ПС. С увеличением времени анодирования независимо от плотности тока

формируется двухслойная структура с внутренним древовидным слоем пористого кремния, вклад которого в фотолюминесценцию минимален, а коэффициент отражения сильно падает из-за безвозвратных потерь в пористый древовидный слой.

Ключевые слова: кремний, встроенный *p–n* переход, плотность тока, время анодирования, освещенность

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Introduction

For anodizing n-type silicon wafers, regardless of their electrical conductivity, it is necessary to ensure the generation of holes, which are minority carriers. This can be done in two ways [1]: either by applying a critical electric field to induce electrical breakdown, or by illuminating with radiation sufficient to generate holes due to the photoelectric effect [1]. It is known that IR illumination from the reverse side of the substrate provides the generation of electron-hole phases, their separation, and diffusion of holes to the front side of the substrate that is under the action of a negative potential, which in turn leads to formation of macroporous structures during anodization [1, 2]. However, under conditions of illumination from the front side of the silicon substrate [3], depending on the parameters of anodization and the degree of its doping, the formation of a two-layer structure was observed, consisting of a thin nanoporous layer and a thicker macroporous layer. However, complex studies of anodization in silicon with a built-in *p–n* junction, to our knowledge, have not been previously carried out.

Experimental

For anodizing, single-crystal silicon Si(100) wafers of *n*-type conductivity with an epitaxial layer of *p*-type conductivity were used. Layers of porous silicon (por-Si) were formed at two anodizing current densities (10 and 20 mA/cm^2) and etching durations from 10 to 30 minutes, as well as using illumination with a 150 W tungsten lamp during the anodizing process.

A home-made Teflon attachment with a platinum wire cathode was used for anodizing and a copper anode, which was pressed through a layer of conductive silver paste to the reverse side of the silicon sample with the burnt Au-Sb contact. The edges of the front surface of the sample with an area of up to 1 cm^2 were protected with a special varnish. After anodizing, the samples were washed in deionized water and dried in a flow of dry nitrogen.

After mechanical removal of varnish residues and wiping with isopropyl alcohol, a porous silicon layer was studied by optical reflectance and photoluminescent (PL) spectroscopies, as well as by scanning electron microscopy (SEM), including cross-section images for porous structures [4]. During anodization, 8 samples of por-Si were formed with two current densities and different anodization durations.

Results and Discussion

When anodizing with a current density of 10 mA/cm^2 for up to 15 minutes (sample 2-5), the formation of a relatively homogeneous por-Si layer with a low density of punctures is observed. The overall thickness of PS layer is about 0.72 μm (Fig. 1, *a*). It consists of two parts. The lighter part is closer to the surface. Its thickness is about 0.56 μm (Fig. 1, *a*). The darker part with a thickness of 0.16 μm lies under the top layer at the interface with single-crystal silicon. The color of the porous silicon layer is light, which corresponds to a weak absorption of electrons and, accordingly, its low porosity. The darker part of the porous layer should have a higher porosity.

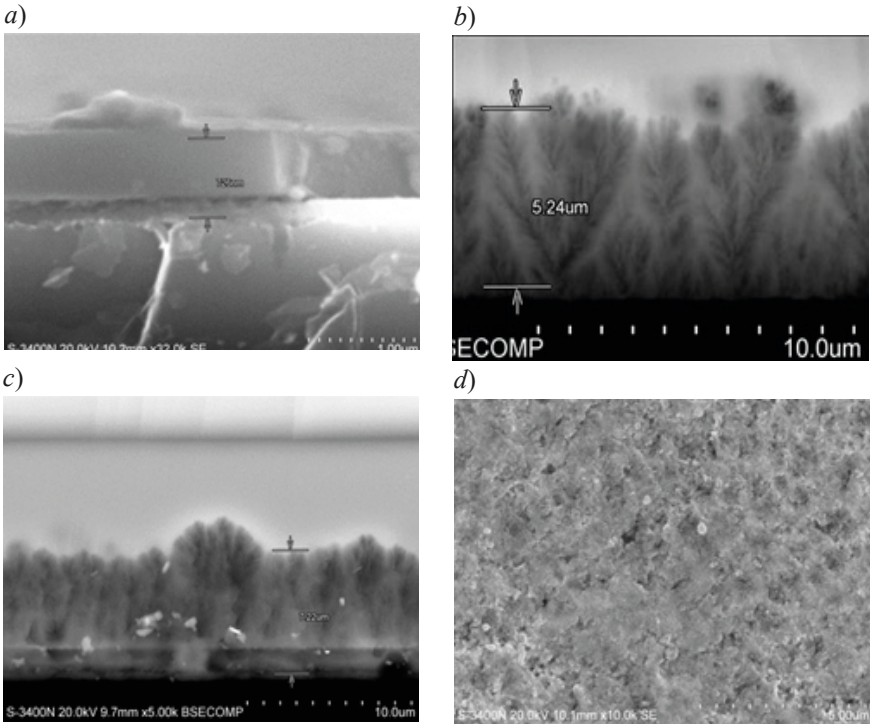

Fig. 1. SEM cross-section images of porous silicon (PS) layers on Si substrate with a *p–n* junction formed at anodizing current density of 10 mA/cm^2 and different anodizing times: 15 minutes for sample 2-5 (*a*); 25 minutes for sample 2-6 (*b*) and 30 minutes for sample 2-2 (*c*). A surface image of PS layer (sample 2-6) after 25 minutes of anodizing is also shown (*d*)

Increasing the anodization time to 25 minutes and then to 30 minutes led to the formation of a por-Si tree-like porous structure inside silicon with an increase in the total por-Si thickness from 5.2 μm to 7.2 μm (Fig. 1, *b, c*). After 25 minutes of anodizing, a certain disturbed layer with a network of small punctures (Fig. 1, *b*) covering the underlying tree-like porous structure is observed on the surface of the porous layer (sample 2-6). Such a disturbed layer is always or often formed over a por-Si layer [5]. After 30 minutes of anodizing (sample 2-2), the thickness of the tree-like porous layer increased (Fig. 1, *c*), but the thickness of the damaged layer also increased to about 2 μm. The upper (disturbed) layer has a darker color, which corresponds to its higher porosity.

The photoluminescence (PL) spectra from the formed samples with porous silicon were studied at room temperature and two laser lines: $\lambda = 405$ nm and $\lambda = 532$ nm.

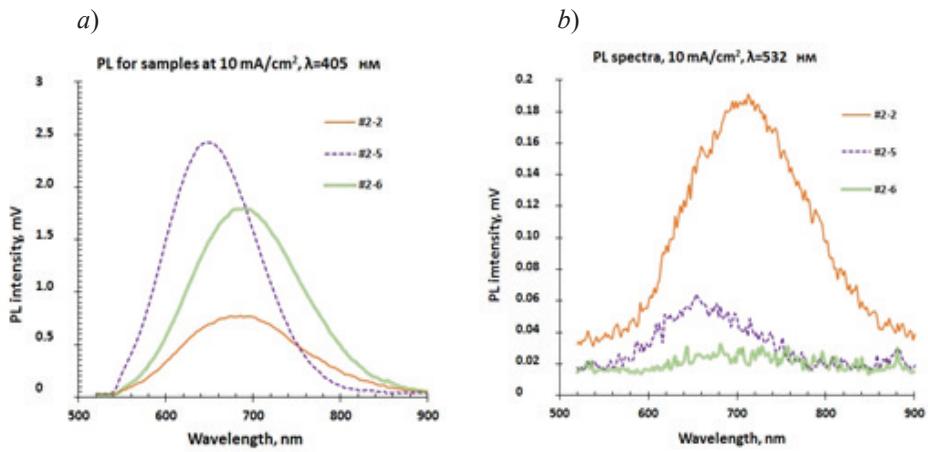

Fig. 2. Photoluminescence (PL) spectra of por-Si layers at different laser wavelengths: 405 nm (*a*) and 532 nm (*b*) for samples formed at anodizing current density of 10 mA/cm^2 and different anodizing times: 15 minutes (sample 2-5), 25 minutes (sample 2-6) and 30 minutes (sample 2-2)

The maximum intensity of the PL spectrum at $\lambda = 405$ nm was observed for the PC layer with an anodizing time of 15 minutes (sample 2-5, Fig. 2, *a*), which indicates high porosity [3] of the internal porous layer (Fig. 1, *a*) and the generation of the PL signal only in this thin internal por-Si layer. With an increase in the anodizing time (samples 2-6 and 2-2), the PL spectra decreased in intensity and red-shifted. With an increase in the laser wavelength ($\lambda = 532$ nm, Fig. 2, *b*) and hence the depth of penetration into the por-Si layer, the intensity of the PL spectra strongly decreased for all samples (Fig. 2, *b*). At the same time, the maximum intensity and red shift of the spectrum was exhibited by a sample with an anodizing time of 30 minutes. This indicates the main contribution to the PL spectrum from the near-surface PS layer for samples 2-6 and 2-5. However, for sample 2-2, the decrease in the PL intensity at $\lambda = 532$ nm is noticeably smaller, and the red shift is larger than for the other two samples (Fig. 2, *b*), which is associated with a larger thickness of the damaged layer and its lower porosity.

Recording the reflectance spectra in the UV-VIS range showed (Fig. 3) that a sharp decrease in reflection is observed over the entire range in layers with a tree-like structure (samples 2-2, 2-6), which indicates an increase in irretrievable light losses in such layers. Noticeable interference features in the reflection spectra (Fig. 3) for samples 2-2 and 2-6 indicate that the por-Si layer remains sufficiently flat. At the same time, the high reflectance for sample 2-5 (15 minutes) corresponds to the preservation of the flat surface of the por-Si layer. Taking into account the noticeable blue shift of the PL spectrum (Fig. 1, *a*) in the sample 2-5, we can suggest the small sizes of Si nanocrystals internal porous layer with a high porosity [3]. The small thickness of porous silicon in sample 2-5 is confirmed by the appearance of peaks from single-crystal silicon, which are observed in the reflection spectrum of this sample at wavelengths of about 270 nm and 360 nm (Fig. 3).

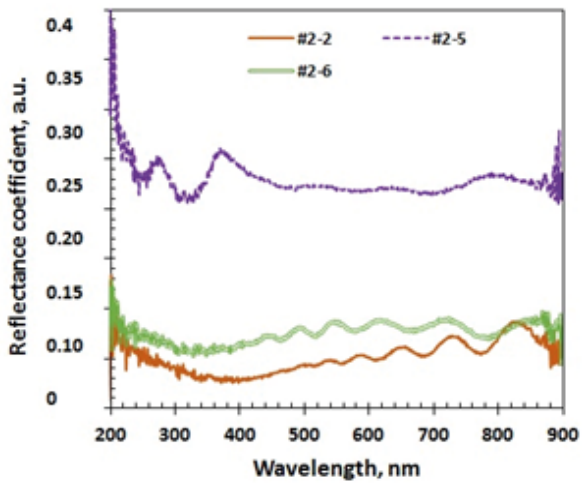

Fig. 3. Reflection spectra of por-Si layers formed at anodizing current density of 10 mA/cm^2 and different anodizing times: 15 minutes (sample 2-5), 25 minutes (sample 2-6) and 30 minutes (sample 2-2)

An increase in the anodization current density to 20 mA/cm^2 led to the formation of a two-layer por-Si structure, which includes a thin homogeneous PS layer (Fig. 4, *a*, sample 2-3) and then a tree-like structure (samples 2-4 and 2-10). The thickness of the entire por-Si layer increased with the etching time (10, 15, 30 min) from 1.67 μm to 16.7 μm.

The position of the maximum in the PL spectra practically did not depend on the anodizing time, and the intensity of the PL peak decreased with increasing anodizing time, which is confirmed by a decrease in the PL intensity upon going from $\lambda = 405$ nm to $\lambda = 532$ nm and PL localization mainly in the upper por-Si layer, but with variable porosity. Porosity turned out to be maximum for the minimum of anodizing time (see samples 2-3 and 2-9 with 10 minutes of anodizing time).

The reflection spectra of the samples of the second series with an anodizing current of 20 mA/cm^2 showed that in the samples with the maximum PL intensity (2-3 and 2-9) with a minimum anodizing time (10 minutes), intense interference peaks are observed (Fig. 6), despite the small thickness of the upper por-Si layer (Fig. 4, *a*). This means that a certain contribution is made by the inner layer with a tree structure and different porosity. The upper flat layer with low porosity is retained in samples 2-4 and 2-10 with a greater thickness of the inner tree-like layer, which determines a greater reflection coefficient. This is confirmed by the presence of peaks from single crystal silicon at wavelengths of 270 nm and 370 nm.

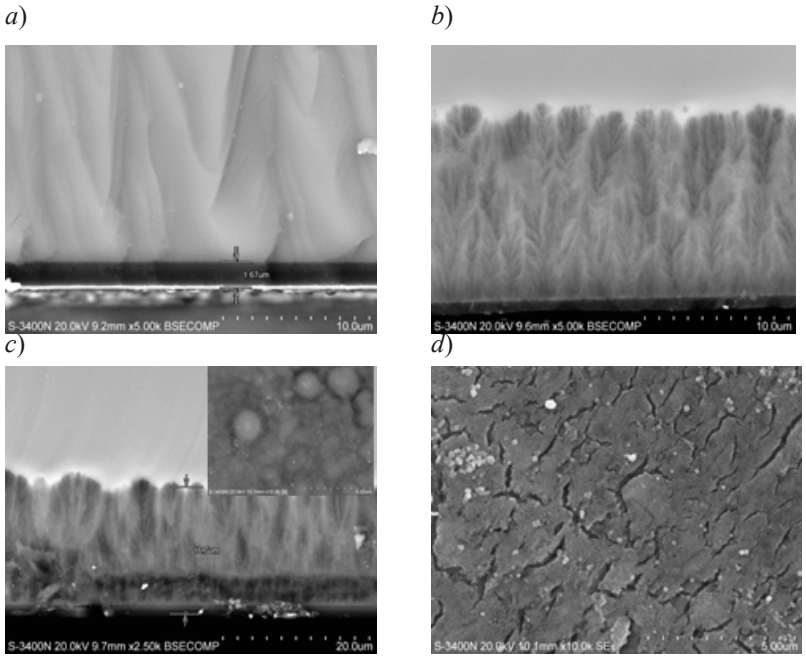

Fig. 4. SEM cross-section images of porous silicon (por-Si) layers on Si substrate with *p–n* junction formed at anodizing current density of 20 mA/cm^2 and different anodizing times: 10 minutes for sample 2-3 (*a*); 15 minutes for sample 2-10 (*b*) and 30 minutes for sample 2-4 (*c*). A surface image of PS layer (sample 2-10) after 15 minutes of anodizing is also shown (*d*). The inset in (*b*) corresponds to the sample surface.

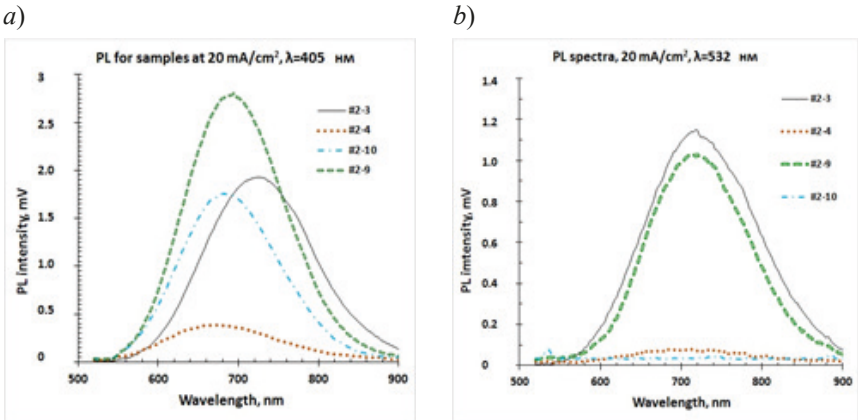

Fig. 5. Photoluminescence (PL) spectra of por-Si layers at different laser wavelengths: (*a*) λ =405 nm and (*b*) λ =532 nm for samples formed at anodizing current density of 20 mA/cm2 and different anodizing times: 10 minutes (samples 2-3 and 2-9), 15 minutes (sample 2-10) and 30 minutes (sample 2-4)

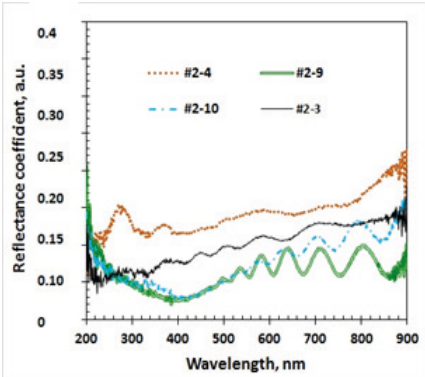

Fig. 6. Reflection spectra of por-Si layers formed at anodizing current density of 20 mA/cm^2 and different anodizing times: 10 minutes (samples 2-3 and 2-9), 15 minutes (sample 2-10) and 30 minutes (sample 2-4)

Conclusion

The effect of anodizing modes (anodizing current and duration) on the formation of porous silicon layers in a Si-*p*/Si-*n* epitaxial structure under conditions of white light illumination has been studied. It has been established that at short anodization times of 10 minutes at 10 mA/cm^2 and 15 minutes at 20 mA/cm^2, an upper porous layer with a noticeable porosity is formed, which ensures strong photoluminescence (PL), which is more pronounced at a laser excitation length of $\lambda = 405$ nm and decreases noticeably at $\lambda = 532$ nm. With an increase in anodizing time (20–30 minutes), a tree-like porous layer is formed inside under the first layer of por-Si, the thickness of which increases with an increase in anodizing time and anodizing current density. The photoluminescence in the double porous structure decreases with an increase in the anodizing time. In this case, the PL intensity from thick tree-like layers is minimal at a laser radiation length $\lambda = 532$ nm. The reflection coefficient in samples with a double porous structure becomes less than 0.1, if the upper layer of the por-Si is highly porous and does not retain the contribution from single-crystal silicon.

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THE AUTHORS

YAN Dmitriy T.
dmitry_yan@mail.ru
ORCID: 0000-0002-0602-9301

GALKIN Konstantin N.
galkinkn@iacp.dvo.ru
ORCID: 0000-0001-5386-1013

GALKIN Nikolay G.
galkin@iacp.dvo.ru
ORCID: 0000-0003-4127-2988

NEPOMNYASHCHIY Aleksandr V.
santila001@mail.ru
ORCID: 0000-0002-8726-983

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