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SUBSTRATE CRYSTALLOGRAPHIC ORIENTATION EFFECT ON PHOTOLUMINESCENT PROPERTIES OF POROUS SILICON

Etching duration and anodic current density dependences of intensity and maximum position of the photoluminescence spectra of porous silicon layers obtained by anodization of silicon wafer are investigated. The sizes of silicon nanoclusters formed during the anodization procedure are estimated. It is shown that the dependence of formed clusters sizes on etching conditions for porous layers is different for various crystallographic orientations of the substrate. The model explaining this feature at various speeds of porous layer frontal advance deep into silicon substrate is offered. Presented results may be used for optimization of etching conditions in order to obtain the porous silicon layers having the preset parameters.

1. INTRODUCTION

Silicon is the basic material for modern electronics — that is why new silicon-based substances employed in micro- and optoelectronics are cheaper. This fact is substances for needs of micro- and optoelectronics on its basis result cheaper due to use of standard technological processes by their fabrication. Taking into account the recent tendency to transform microelectronics into nanoelectronics (i. e. into technology of submicronic spatial scales) and hence to explore the arising quantum effects, the study of properties typical of nano-size structures on the basis of silicon becomes especially actual. Porous silicon is the most promising similar medium [1]. Nano-size silicon clusters, formed in the porous layer, produce the efficient visual photoluminescence of a material due to the occurrence of the quantum confinement effect [2]. The mechanism of this photoluminescence has been studied intensively [3—4] and at present, the issue how to increase its quantum yield, is rather pressing problem in micro- and nanoelectronics.

Physical properties of the porous silicon layers, obtained in anodic electrochemical etching of silicon wafers, depend directly on anodization parameters [1, 5]. Besides, such properties of the initial material, as type of conductivity, doping level, substrate crystallographic orientation and surface condition, deeply influence results of anodization. Substrate crystallographic orientation effect on photoluminescent properties of the porous layers formed as a result of anodization with different etching duration and at various anodic current densities is investigated in the present paper.

2. EXPERIMENTAL PROCEDURE

P-type silicon wafers with thickness 450 μm, specific conductivity 10 Ω·cm and crystal orientations (111) and (100) were used as the initial material. The anodization was realized at room temperature without accent lighting in electrochemical cell consisting of two cylindrical chambers. One of the chambers was filled with NaCl water solution, and a copper electrode was located into it. A platinum electrode was located in the second chamber which, in turn, was filled with etching agent composed of 1:1 ($HF(49\%):C_2H_5OH$). A sample, clamped between two plexiglas plates with round windows, was located between the chambers of electrochemical cell. Rubber linings were used as sealants. The voltage from stabilized power source was applied to the cell electrodes. The anodic current density varied from 5 mA/cm² up to 40 mA/cm². Etching duration varied from several minutes up to one hour. The received samples were seasoned on open air within one week for stabilization of created porous layers.

A standard set-up [6] was used to study of anodization parameters effect on the spectra of the obtained porous samples photoluminescence. Excitation was realized by pulse nitrogen laser with wavelength of 337 nm, pulse duration of 10 ns, recurrence frequency of 50 Hz and average capacity 3 mW.

3. RESULTS AND DISCUSSION

As is known [1, 4], the porous layer, which was formed due to the silicon wafers anodization, contains nanocreations. This fact results in the presence of the quantum confinement effect and, as a consequence, in the appearance of photoluminescence in the visible part of spectrum [1, 7]. The photoluminescence spectra recorded by us had the typical Gauss-like shape with one peak only for all samples, irrespective of substrate crystallographic orientation and anodization parameters (Fig. 1). The typical sizes of above-said clusters may be calculated from spectral positions of the photoluminescence maxima by the adjustment of experimental spec-

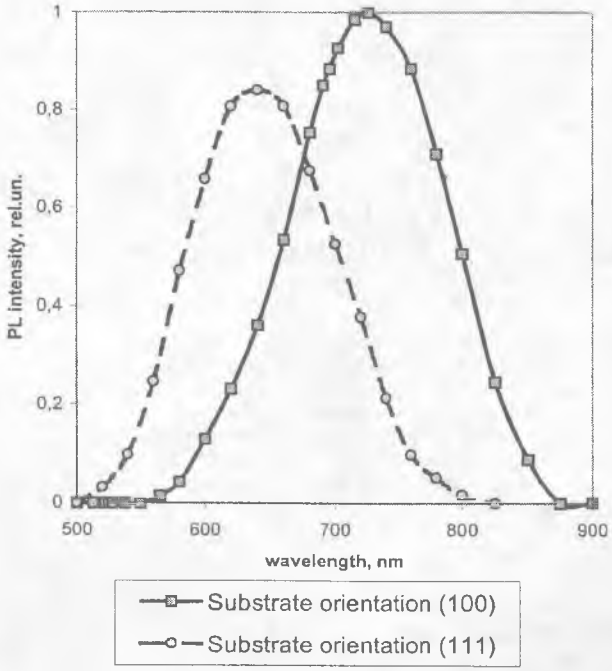

Fig. 1. PL spectra of silicon porous layers obtained at 20 min. anodization by 7 mA/cm2

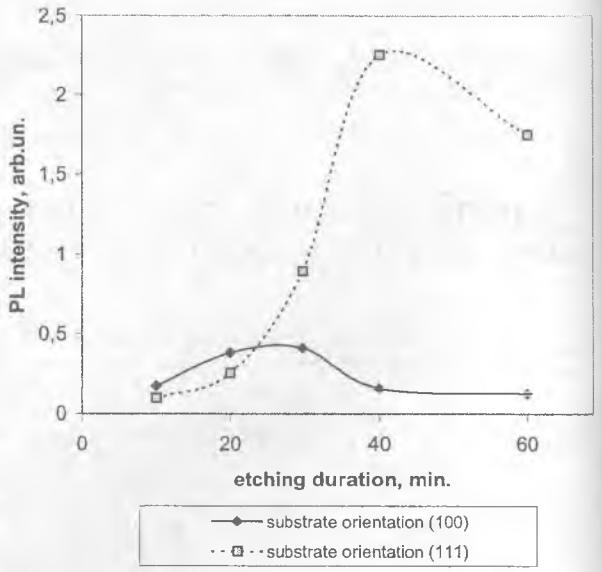

Fig. 2. Etching duration effect of porous silicon photoluminescence intensities at constant anodic current density 7 mA/cm2

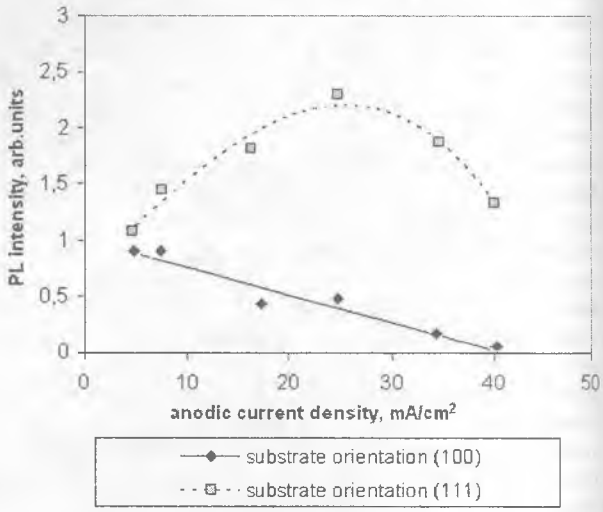

Fig. 3. The anodic current density effect of porous silicon photoluminescence intensities at 40 min. etching duration

tra with Gaussian [8]. Spectral position of the maximum can change in a quite wide range with the variation of etching duration and anodic current density.

To estimate the anodization parameters variation effect on the photoluminescence efficiency of porous silicon, the dependences of photoluminescence intensities on etching duration at constant anodic current density of 7 mA/cm^2 (Fig. 2) and on anodic current density at 40 minutes etching duration (Fig. 3) for both considered substrate crystallographic orientations were plotted. Figure 2 shows that at substrate orientation (111) the photoluminescence intensity is maximal at 40 minute etching. For the porous layers created on the substrate with crystallographic orientation (100), the photoluminescence intensity reaches the maximal value earlier, but decreases more abruptly. Let us note that we succeeded to achieve higher quantum yield of luminescence for layers on the substrate with orientation (111). This effect is explained below.

At varying of anodic current density the pronounced maximum of photoluminescence intensity is observed for porous layers on the substrate with orientation (111). An increase in current density should be accompanied by an increase in photoluminescence intensity because of nanoclusters formation and their simultaneous reduction due to chemical irritation of clusters already formed. The competition between those processes results in the specified maximum. At substrate orientation (100) the increase of anodic current density results in the luminescence quantum yield reduction with almost the linear law (Fig. 3). Hence, chemical irritation of clusters begins at very low current density in this case (practically at once).

Dependences of the typical silicon clusters sizes on etching duration (Fig. 4) and on anodic current density (Fig. 5) were investigated using the adjustment of experimental photoluminescence spectra with Gaussians [8]. It is visible from the specified dependences that the typical silicon clusters' size increases at increasing both etching durations and current density for the porous silicon layers created on the substrate with crystallographic orientation (100). An inverse picture is observed for the porous silicon layers created on the substrate with crystallographic orientation (111): at increase in varied anodization parameters causes the reduction of the typical clusters size.

The analysis of the data, performed by fitting experimental photoluminescence spectra with Gaussians, allowed us to estimate the sizes of silicon clusters created during porous layers for-

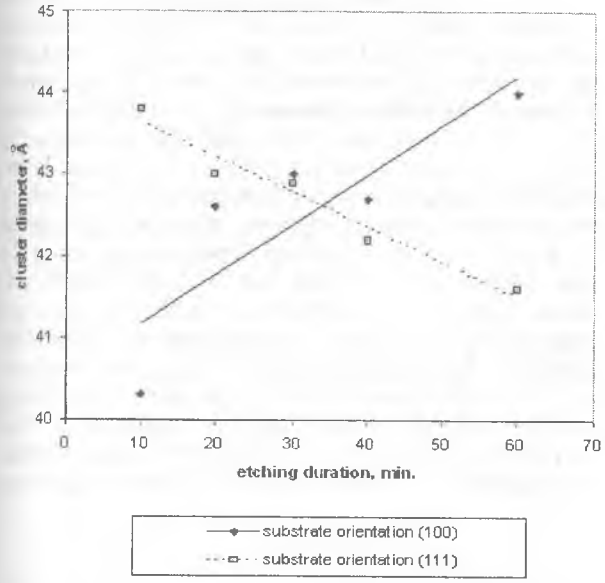

Fig. 4. Dependences of the typical silicon clusters sizes in porous silicon on etching duration

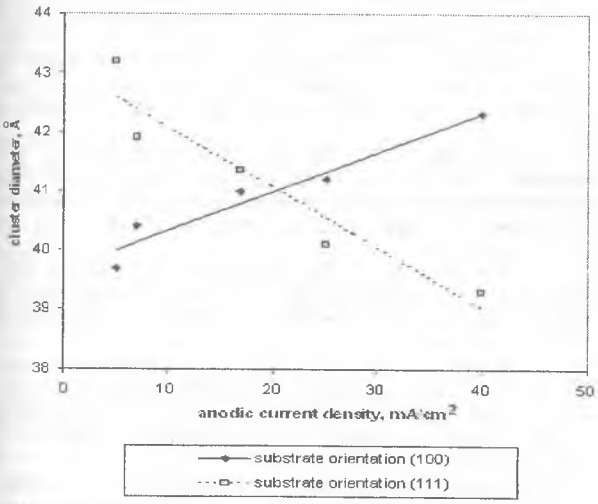

Fig. 5. Dependences of the typical silicon clusters sizes in porous silicon on anodic current density

mation in the anodization process on substrates having crystallographic orientation (111) and (100). Figure 6 shows the projections of the diamond structure, in which silicon crystallizes, on (111) plane (*a*), and on (100) plane (*b*). The black circle shows the silicon atom situated in the plane of figure, the grey circles show distant atoms, whereas white circles show even more distant atoms. Those parts of intercrystalline space of the ideal silicon crystal where it is most probable to find an electron (at ground electronic state) are presented by solid or dashed lines. These lines correspond to bonds between silicon atoms. It turns out that the electrons never reside in the geometrical center of «gaps» between atoms (rhombuses in Fig. 6,a or squares in Fig. 6,b), because the charge density is zero there. Therefore it is energetically preferable for the etching agent ions that are directed by the

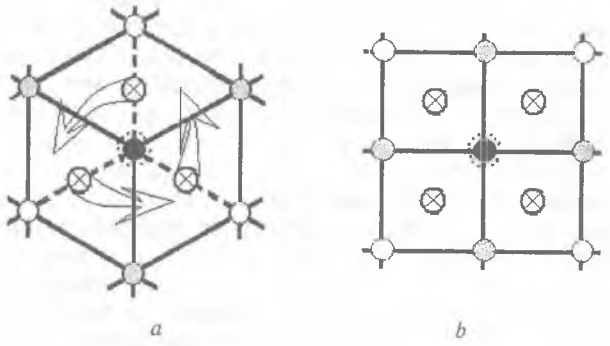

Fig. 6. Projections of diamond lattice (O_h^7) onto:

a — crystallographic plane (111); *b* — crystallographic plane (100). Dotted circle shows the impurity position. Crosses in circles and arrows show the etching agent stream direction

electric field perpendicularly of figure plane, to be situated in the «gaps» geometrical center.

For boron-doped silicon wafer, very small impurity atoms are shown in Figure 6 as dotted circles and situated under the black circles, directly where the interstitial spaces are. Reaching inside a wafer, the etching agent ions may interact with boron impurity and its displacement from interstitial space will liberate 2.25 eV of energy as it is well known. This energy will be used for loosening a lattice, deviation and extension of bonds (are designated on Fig. 6 by solid and dashed lines) so that weakened Si-Si bonds are destroyed too. In this way the nanoformations are appearing in the porous layer.

For the wafer orientation (100), as it is shown in Fig. 6, the stream of the etching agent ions (criss-crossed in the circle) will be situated in the geometrical centers of «squares», and so it will completely penetrate the structure. Certainly, the etching of boron atoms and the accompanying processes described above will occur too, but nothing will prevent the etching agent from frontal advance deep into wafer, and thus the acceptor atoms will be aside a little. While etching silicon wafers with crystallographic orientation (111), the stream of the etching agent ions will situate in the geometrical center of «rhombuses», but passing a small distance of about 8 Å, the stream meets on its way an obstacle, namely a force field created by bonds between the silicon atoms (they are shown by dashed lines on the Fig. 6, *a*) and therefore changes its direction. Actually the stream of the etching agent ions begins to move along a screw line (visualized by arrows), meeting periodically on its way the acceptor atoms (with the period $a/4\sqrt{3}$, where a is lattice constant) and etching them. The etching agent front will advance slowly, but it will cause significant structure destructions. Here, the significant part of anodization energy is dissipated on irritation of the already formed quantum wires. It results in their crushing and, consequently, in an increase in the small-size clusters number, with an increase both in etching duration and anodic current density, for the wafers with orientation (111).

Much faster etching frontal advance deep into the silicon substrate having crystallographic orientation (100) makes the irritation process of created quantum wires less intensive and predominant at the initial stage of pores formation only. Thus, the pores are formed deep enough and have small diameter, so the diffusion processes are less pronounced. The process of both reaction products outflow from formed pores, and the supple of a fresh solution in them, is complicated. Therefore the reaction products containing silicon are accumulated in the etching agent. As a result, the etching agent is exhausted, oversaturated by silicon, and silicon recrystallized from it. This process results in an increase of the average cluster size with longer etching time and higher anodic current density.

The described above model is also confirmed by smaller quantum yield of luminescence for the porous layers formed on substrates having crystallographic orientation (100) in comparison with layers on substrates having crystallographic orientation (111). Figures 2 and 3 illustrate this fact. There are a smaller number of nanocreations in porous layers on substrates with orientation (100) but, as follows from the model, these creations have larger sizes. The effective surface of luminescence is smaller in this case too, and thus its total intensity is lower [7].

4. CONCLUSION

Photoluminescence intensity of the porous layers obtained on silicon wafers, having crystallographic orientation (111), is maximal at 40 minute etching. The photoluminescence achieves the maximal intensity earlier for the porous layers created on the substrate with orientation (100), but it decreases more abruptly.

With the increase in both etching duration and anodic current density there is an increase in the typical clusters size for the porous silicon layers created on the substrate with crystallographic orientation (100). For the porous layers created on the substrate with crystallographic orientation (111), there is a reduction of the typical clusters size at same conditions.

We explain the observed tendencies in the following way. The stream of electrolyte directed by the electric field meets on its way an obstacle in the form of the force field created by bonds between the silicon atoms at the wafer orientation (111), whereas this specified obstacle is absent at the orientation (100). The porous layer frontal advance deep into the silicon substrate is complicated in the first case, while a high speed of progress of the etching front corresponds to the second case. At the fast etching frontal advance there is a depletion of etching agent, accompanied by silicon recrystallization from the solution. As a consequence, there is an increase of the cluster size. The low speed of the etching frontal advance results in the irritation of the formed quantum wires, in their crushing and, accordingly, in an increase in the small-size clusters number.

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