The influence of technological parameters on the optical properties of photosensitive structures based on porous silicon

To cite this article: N Latukhina et al 2018 J. Phys.: Conf. Ser. 1096 012124

View the article online for updates and enhancements.
1. Introduction

Photosensitive structures that use layers of porous silicon (por-Si) used show increased spectral sensitivity in the short-wave part of the spectrum, thus increasing the efficiency of the silicon solar cells. However, the properties of porous silicon strongly depend on the technological parameters of their fabrication, and the creation of photosensitive structures is associated with performing such a complicated technological operation as diffusion, with the formation of a p-n junction. The purpose of this work was to investigate the effect of the diffusion procedure on the properties of photosensitive structures with porous silicon as the working layer.

Photosensitive structures were created in two ways. In one case, the porous layer was created on plates with a ready p-n-junction (Fig.1). The initial templates were wafers of monocrystalline silicon of p-type conductivity with a polished, ground or textured surface, which is an array of regular tetrahedral pyramids [1]. Phosphorus was diffused into the substrate, resulting in a structure with a shallow p-n junction. Then, by electrolytic etching, the porous layer was formed on the surface of the wafer. As a result of etching of structures with a shallow p-n junction, the original n-type conductivity on the faces of the tetrahedral vertices is preserved. Since the formation of pores occurs at the points of contact of the bases, the formed structure is a series of vertical diodes connected by a common substrate of the p-type conductivity. A similar pattern is observed for the ground surface: pore formation occurs in the depressions of the microrelief, on the elevations the p-type conductivity is conserved (Fig.1a). For a polished surface, this effect is practically not observed, etching occurs evenly over the entire surface.

In the second case, the diffusion of the donor impurity was carried out into the already formed porous layer of the p-type conductivity. The entire developed surface of the porous layer acquires n-type conductivity, forming a large-area p-n junction. However, it was shown in [2, 3] that the melting temperature of porous silicon is substantially lower than that of a monocrystalline.
Thus, there is a danger of destroying the nanocrystalline structure of the porous layer during the procedure of high-temperature diffusion.

In this work we investigated the morphology, optical and photoelectric properties of photosensitive structures with a porous layer, manufactured in two ways: with porosity before and after diffusion, although the diffusion procedure itself was carried out under the same conditions.

2. Experimental technique

The porous layer is formed in a hydroalcoholic solution of hydrofluoric acid by electrochemical etching in a cell of a vertical type. We used single-crystal silicon wafers with different surface microreliefs: ground, polished, and textured. The P-n-junction was created by phosphorus doping at a temperature of 1000°C in an air atmosphere.

The morphology of the samples was studied on a FEI Quanta 200 scanning electron microscope.

The measurements included the measurement of the reflection coefficient and the photosensitivity of the structures.

The spectral dependences of the reflection coefficients were studied using a Shimadzu UV-2450 spectrophotometer with a prefix 206-14046 [4]. The measurement range was 0.3 - 1 µm, the measurement step and the spectral width of the monochromator slit were 2 nm, the scanning rate was slow. The angle of radiation incidence having an elliptical polarization of about 3: 1 - 4: 1 was 5° with an aperture of not more than 5°. The radiation receiver of the Shimadzu UV-2450 spectrophotometer is a photoelectric multiplier. This causes significant noise measurements of the instrument in the near infrared region.

Quantum efficiency was measured using a QEX10 unit from PV Measurements, Inc. in Research and Development center for thin-film technologies in energetics (St. Petersburg), the remaining measurements were conducted in the laboratories of Samara University.

Investigation of photosensitivity was carried out on a measuring stand, which included a mercury lamp, a monochromator and a sensitive microammeter. Photosensitivity was determined taking into account the spectrum of the lamp as the ratio of the photocurrent to the power of the incident radiation. All measurements were carried out in air at room temperature.
3. Results

3.1. Spectral dependences of the reflection coefficient

Figures 2-4 show the spectral dependences of the reflection coefficient for solar cell samples before and after diffusion on different types of working surface.

It can be seen from graphs 2-3 that the formation of a porous layer significantly reduces the reflection coefficient, while the course of the curves of the spectral dependences remains almost unchanged, which is explained by the local nature of pore formation [5].

However, after carrying out diffusion on all types of surfaces of solar cells, the value of the reflection coefficient increases significantly and becomes higher than the original sample without a porous layer [6-8]. For polished structures, this dependence is more pronounced. The reflection coefficient varies by 5-7% of the original sample. For other types of surfaces, this difference varies in fractions of a percent. This can be explained by the change in the porous layer as a result of the high-temperature action during diffusion, i.e. reflow of the pore walls, as well as the presence in the pores of the remnants of the diffusant with a high reflection coefficient.

Analysis of the data on the reflection coefficient measured on samples with different electrolytic etching times shows that it varies in different ways depending on the relief of the initial surface. For samples with original ground or polished surface of the lowest values are reflectance samples with the etching time 10 min. When the time is increased to 15 minutes, the etching goes into the electropolishing mode, the relief is smoothed, which leads to an increase in the reflection coefficient. For a textured surface, an increase in etching time of up to 15 minutes leads to the fact that dissolution of facets of pyramids with high reflectivity begins, so the reflection coefficient continues to decrease (Fig.1 b).

![Figure 2](image)

**Figure 2.** The spectral dependence of the reflection coefficient of textured samples with a porous layer formation before and after diffusion at different etching times: a) 5 min; b) 10 min; c) 15 min.
3.2. Spectral dependences of the photosensitivity

Figures 5 a, b show the spectral dependences of the photosensitivity of the samples with pore formation before and after diffusion at different etching times.

It can be seen from the figure that the curves of dependencies for two different types of structures are completely different in character. The structures of the first type with pore formation before diffusion have an increased sensitivity in the short-wave part of the spectrum, which is associated with the presence of silicon nanocrystals or amorphous silicon in the pores. Hence it can be concluded that the assumption of the destruction of the nanostructure of porous silicon during high-temperature diffusion is not confirmed.

However, a more plausible explanation may be that the increased photosensitivity in the short-wave part of the spectrum is associated not so much with silicon nanocrystals as with amorphous silicon, which does not degrade under high-temperature diffusion.

Structures of the second type with pore formation after diffusion of this behavior do not manifest themselves in the majority, which may indicate the absence (at least on the surface)

![Figure 3](image_url)

**Figure 3.** The spectral dependence of the reflection coefficient of ground samples from the porous layer formation before and after diffusion at different etching time: a) 5 min; b) 10 min; c) 15 min.
of the nanostructure or amorphous silicon. This can be explained by the fact that the diffusion of the dopant passes through the vacancies of the structure, and if pore formation occurs after it, the free vacancies serving as centers of nucleation are much less than in the case of pore formation before diffusion. In this case, the overall value of the photosensitivity for structures of the second type is much higher, since fusion of pore walls and the presence of diffusant residues in them is not present in this case.

Analysis of the photosensitivity data for samples with different electrolytic etching times shows that for each type of surface to be treated, there is an optimum etching time.

For samples with a textured and ground surface with pore formation to diffusion, the optimum etching time was 10 minutes [1]. While samples with a ready p-n junction on a textured surface with an increase in etching time of up to 10 minutes became less sensitive. This can be explained by washing out the doping impurity and, correspondingly, by increasing the resistance of the upper absorbing layer of the n-type conductivity structure [9].

3.3. Spectral dependences of the quantum efficiency

Figure 6 shows the spectral dependence of the quantum efficiency of samples of solar cells fabricated on a textured surface with porosity before and after diffusion.

![Figure 4](image)

**Figure 4.** The spectral dependence of the reflection coefficient of polished samples with a porous layer formation before and after diffusion at different etching times: a) 5 min; b) 10 min; c) 15 min.

It can be seen from the figure that the quantum efficiency is higher for those samples in which pore formation occurred after diffusion. The difference in quantum efficiency is 17-20%.
4. Conclusion
Thus, the conducted complex of studies has shown that the creation of photosensitive structures with a porous working layer on a silicon substrate is possible in two ways: with pore formation before and after the diffusion of the dopant. Both methods lead to the formation of a structure
with a pn junction, but in the second case, the photosensitivity is higher.

This allows us to conclude that the process of diffusion of a dopant into a porous layer passing at a temperature of 1000°C negatively affects the optical and photoelectric properties of structure with any type of initial surface, increasing the reflection coefficient and reducing the photosensitivity. However, this effect is most noticeable on structures fabricated on plates with a polished surface due to the features of pore formation and diffusion of the impurity into the porous layer on such a surface. Structures with pore formation after diffusion do not experience such influence. A disadvantage of such structures is the relatively high electrical resistance of the upper layer due to partial outwashing of the dopant during electrolytic etching to form a porous layer. When using such structures in solar cells, this problem can be solved by applying a layer of a conductive coating such as zinc sulphide.

5. References
[1] Latukhina N V 2015 Procedia Engineering 104 157
[2] Yang C C 2003 J. of Physics: Condensed Matt. C 15 4961
[3] Timoshenko V Yu 2000 Phys. Status. Sil. A 182 325
[4] Paranin V D and Karpeev S V 2016 Computer Optics 40(1) 36-44 DOI: 10.18287/2412-6179-2016-40-1-36-44
[5] Latukhina N V 2017 CEUR Workshop Proceedings 1900 84
[6] Wautelet M 1991 J. Physics: Appl. Phys. D 24 343
[7] Wen Z 2000 J. Physics CCL Condensed Matt. 12 8819
[8] Wautelet M 2004 J. Physics: Condensed Matt. C 16 163
[9] Shalav A 2005 Appl. Phys. Lett. D 86 013505