Photovoltaic characteristics of structures with porous silicon obtained by various technological plans

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Abstract. In this work, the influence of technological parameters on the current-voltage characteristics of solar cells with porous silicon is investigated. It is shown that for photosensitive structures with a porous layer, the optimal mode is pore formation by electrochemical etching followed by diffusion. The effect of etching modes affects the character of the photosensitivity curve.

1. Introduction
Currently, alternative energy sources are becoming more and more relevant. This is due to many factors. In particular, the main sources of energy, such as oil, gas, coal, etc., are non-renewable. Their reserves are gradually being depleted, and sooner or later the time will come when they will have to be abandoned. In addition, their extraction is dangerous for the environment. For example, the high consumption of oil and petroleum products has led to the need to extract raw materials such as bituminous sands. But their development causes great harm to the environment: oil obtained from bituminous sands produces three times more carbon dioxide than with traditional drilling; the open-pit method involves deforestation and the removal of up to several tons of soil and peat; the waste water of the quarry can seep into the environment and pollute the groundwater.

Most coal-fired power plants are located in the immediate vicinity of the mines. This is due not only to the destruction of the natural environment by the hectares of workings created by the mines, but also to the air pollution in this region with carbon dioxide, sulfur dioxide, nitrogen oxide and dust. The electrostatic filters and chimneys of powerful power plants do not stop the release of toxic chemical compounds that cause damage to agricultural land and forests in nearby regions. Creating such large open spaces also requires appropriate adaptation of the terrain and the environment.

The process of hydraulic fracturing (FRACKING) raises the greatest doubts about the entire technology of shale gas production and is criticized not only by environmentalists. Fracking involves injecting a mixture of water, sand, and chemicals under high pressure into a well and into a closed rock containing natural gas. Energy companies are protected from disclosing what chemicals are used in the fracking process.

As a result, alternative energy sources are used, such as the movement of water in rivers (hydroelectric power plants), kinetic wind energy (wind power plants) and electromagnetic radiation from the Sun (solar power plants). In the field of solar energy, solar photovoltaic installations are considered more profitable, due to the direct conversion of solar radiation into electricity using solar panels, which are a combination of semiconductor photovoltaic converters. It is shown in [1] that the use of porous silicon as a working layer can increase the efficiency of solar cells. However, the
different order of technological processes can negatively affect the characteristics of structures and, as a result, their efficiency.

2. Materials and methods

Samples of photosensitive structures with a porous layer were divided into two groups. Before creating photosensitive structures, p-type silicon wafers with a textured surface were cleaned in a peroxide-ammonia solution and divided into two groups. In one group of samples, the first stage was diffusion at 1000°C, the exposure time was 1 hour.

The porous layer was created in two ways: by electrochemical etching in a horizontal cell in an alcoholic solution of hydrofluoric acid [2] and by metal-stimulated chemical etching (MACE) [3]. Electrochemical etching modes: time 15 minutes, current density $j=15$ mA/cm$^2$.

A typical MAC etching procedure involves a noble metal that partly covers a Si substrate and an etchant composed of HF and an oxidative agent, such as Fe(NO$_3$)$_3$, KAuCl$_4$, K$_2$PtCl$_6$, and H$_2$O$_2$[4]. The former serves as a local cathode catalyzing oxidant reduction and injecting holes into the Si substrate. The holes transferred from the “cathode” oxidize the Si substrate. The silicon oxide is then dissolved by the acidic etchant. As the process goes on, the Si beneath the noble metal is etched away while the Si surface without any metal is nearly impacted. As a result, the noble metal “drill” into the Si substrate, forming various Si nanostructures.

The chemistry of Si dissolution reactions in the presence of HF and H$_2$O$_2$ include cathodic reactions at the metal interface, which result in hole (h) injection into Si via the following chemical reaction of H$_2$O$_2$ decomposition in HF[5]:

$$H_2O_2 + 2H^+ = 2H_2O + 2h^+ \quad (1)$$

and anodic reactions at the Si interface resulting in Si dissolution in HF

$$Si + 6HF + nh^+ = H_2SiF_6 + nH^+ + [(4 - n)/2]H_2. \quad (2)$$

If $n = 2$, anisotropic etching (Si Back-bond theory—[100] preferential etching)

$$Si + 2H^+ + 2h^+ = Si^{4+} + H_2 \quad (3)$$

$$Si^{4+} + 6HF = SiF_6^{2-} + 6H^+.$$  

If $n = 4$, isotropic etching (or electropolishing)

$$Si + 2H_2O + 4h^+ = SiO_2 + 4H^+ \quad (4)$$

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O.$$  

where $n$ is number of holes per dissolved Si atom.

From the overall dissolution reactions

$$Si + 6HF + H_2O_2 = H_2SiF_6 + 2H_2O + H_2 \quad (5)$$

for anisotropic etching,

$$Si + 6HF + 2H_2O_2 = H_2SiF_6 + 4H_2O \quad (6)$$

for isotropic etching.

As shown in figure 1, the metal particles serve as a redox center and function as a short-circuited galvanic cell with a flux of electrons inside the metal particles, while protons would migrate from the anode to the cathode site outside the metal particles.

In horizontal electrochemical etching, passivation of the silicon surface occurs during anodizing in an aqueous solution of HF and pore formation is observed[6].
Figure 1. Metal-assisted catalytic reactions on bulk Si surface [4].

Figure 2 shows some possible pathways for the reaction involved in porous silicon formation.

During anodic treatment in electrolytes containing hydrofluoric acid, the following reactions occur on the surface of the electrode:

- Electrochemical reaction of the formation of silicon fluoride
  \[ Si + 2HF + 2e^+ = SiF_2 + H_2F, \]  
  \( (7) \)

- Chemical reduction of silicon from silicon bifluoride
  \[ 2SiF = Si + SiF_4 \]
  \[ SiF_4 + 2HF = H_2SiF_6, \]  
  \( (8) \)

- Chemical oxidation of silicon bifluoride to silicon dioxide and its dissolution in hydrofluoric acid
  \[ SiF_2 + 2H_2O = SiO_2 + 2HF + H_2 \]
  \[ SiO_2 + 4HF = SiF_4 + 2H_2O \]
  \[ SiF_4 + 2HF = H_2SiF_6 \]  
  \( (9) \)

Depending on the treatment conditions, one of the reactions (8 or 9) prevails, resulting in either the formation of por-Si (reactions 7 and 8) or electropolishing (reactions 7 and 9).

Figure 3 schematically shows the process of horizontal electrochemical etching of silicon.
The first stage of metal-stimulated chemical etching was AgNO$_3$ deposition. For this purpose, silver nitrate weighing 0.2 g was dissolved in 45.5 ml of hydrofluoric acid HF. The samples were fixed on the bottom of the bath in a horizontal position and then filled with the solution for 3 minutes. Then the samples with the deposited silver on the surface of the plates were placed in a mixture of hydrogen peroxide H$_2$O$_2$ and hydrofluoric acid for subsequent etching for 5 minutes. After etching, the samples are placed in concentrated nitric acid to remove the silver nanoparticles.

The other group had the reverse order of technological processes.

Photosensitivity measurements were made using the MDR-3 diffraction monochromator. The radiation source is a xenon arc lamp of the DKSEL 100 type. The light from the lamp hits the collimator, which creates a focused beam of light that enters the input slot of the monochromator. At the output of the monochromator, we have light of the required wavelength, which, falling on the second collimator, is focused and directed to the sample located in the holder. The signal that occurs when the structure is illuminated is recorded. To register the signal, a voltammeter B7-21A was used, which operated in the ammeter mode (nA).

3. Results and discussions

Figure 4 shows SEM images of structures made by the MACE method (figure 4a) and the electrochemical method (figure 4b).

In the electrochemical method, pores are formed mainly at the joints of the pyramids. With MACE, etching occurs on the entire surface of the pyramids, which allows for better radiation capture.

Figure 5 shows the results of measurements of the current-voltage characteristics of porous structures performed by various methods before diffusion (purple curve) and after diffusion (green curve).
Figure 5. The current-voltage characteristic of photosensitive structures with a porous layer was performed (a) by electrochemical etching in a horizontal cell, (b) by the MACE method, before diffusion (purple curve), after diffusion (green curve).

Figure 6 shows the results of measuring the photosensitivity of porous structures in which pore formation was carried out before diffusion (purple curve) and after diffusion (green curve).

Figure 6. The spectral characteristics of photosensitive structures with a porous layer were performed (a) by electrochemical etching in a horizontal cell, (b) by the MACE method, before diffusion (purple curve) and after diffusion (green curve).

The analysis of the graphs shows that for both methods of manufacturing porous layers, the route by which the porous layer is first made, and then diffusion is carried out, is more effective. If the diffusion is carried out before pore formation, then as a result of etching, active etching of the n-type occurs from the substrate, which negatively affects the main parameters of the solar cell: short-circuit current and no-load voltage. Such a technological route also reduces the spectral sensitivity of the samples.

It was also observed that the method of creating a porous layer affects the characteristics of the solar cell (figure 7).

This is primarily due to the characteristics of the resulting porous layer on the textured surface (figure 7). With the help of MACE, a porous layer is formed over the entire surface of the pyramid, providing better light capture, which affects a higher no-load voltage.

However, in horizontal etching, where the porous layer passes only along the bases of the pyramids, the short-circuit current is higher than in the MACE.
Figure 7. Comparison of (a) current-voltage and (b) spectral characteristics of structures with porous silicon obtained by horizontal etching (green curve) and MACE (purple curve).

The lower short-circuit current in photosensitive structures manufactured by the MACE method is associated with current losses caused by poor contact.

4. Conclusion

Thus, the conducted studies have shown that the optimal technological route is pore formation and subsequent diffusion. However, this technological route requires further refinement, namely, the selection of the optimal mode of diffusion and the reduction of recombination losses.

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