Water Splitting Using Porous Silicon Photo-electrodes for Hydrogen Production

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Abstract. This paper presents the efficiency study results of using gradient-porous silicon structures with different morphology, as photo-anodes for photo-electrochemical dissociation of water. The results of a study of the physicochemical properties of gradient-porous silicon structures show the relatively low cost and simplicity of the technological process, as well as the possibility of forming structures with predefined properties, allow the creation of effective devices for artificial photosynthesis based on porous silicon for subsequent use in hydrogen energy.

1. Introduction
Constantly increasing energy consumption throughout the world leads to the inevitable depletion of various fossil fuel sources. This encourages intensive research for practical application of so-called alternative or renewable energy sources. A special place is given to solar energy efficiency research. It is believed that the main supplier of solar energy will be batteries based on solar cells (SE). Direct conversion of solar radiation into the most convenient for human use electric energy with the help of modern solar cells is approaching its possible limit in efficiency. At the same time, the cost of a unit of generated electricity is already comparable to the same amount of electricity produced by burning coal, which is one of the cheapest fossil sources. In addition, the use of solar cell batteries does not require any special operating costs and, at the same time, does not lead to undesirable pollution of the environment. However, the receipt of environmentally friendly electricity with the help of solar cells is accompanied, by the problem associated with the inconstancy of solar radiation falling on the solar cell battery.

On the other hand, there is a volatility in the consumption of electricity over time. There is a need to accumulate surplus electricity generated at maximum intensity of solar radiation and their use under peak loads or minimum intensity of solar radiation. In this case, the preference should be given to the scheme of accumulation, which would not destroy the level of ecology that was achieved in the production of electricity using solar cells. For such purpose, the use of solar energy for the splitting water to produce and store hydrogen and oxygen is considered. The subsequent use of hydrogen as a fuel, and oxygen as an oxidant in hydrogen fuel cells (for example, PEMFC) will virtually balance the generation and consumption of electricity from solar power plants. At the same time as a result of the application of such a scheme there is no pollution of the environment, as the result of the operation of fuel cells in addition to electricity is water and heat. This work presents the results of development and analysis of the efficiency of gradient-porous silicon structures with variable pore morphology, designed to create photo-electrochemical dissociation devices for water based on photo-electrodes.
2. Artificial photosynthesis of hydrogen fuel

Preservation and accumulation of energy are the most important directions for the successful use of various renewable energy sources and, in particular, the sun in the future. An ideal system will simulate a natural cycle of photosynthesis, but with much greater efficiency. One of the most promising candidates in this regard is hydrogen, since it can be obtained from water by electrolysis. Direct production of hydrogen by splitting water with the help of sunlight has a theoretical efficiency (efficiency) of up to 20% using a unijunction semiconductor electrode. More than 30% can be achieved using multi-converter photoelectric converters, for example, a combination of two semiconductor materials with different band gap widths. In the laboratory conditions, the efficiency is more than 12% and 18% for unipolar or tandem semiconductor electrodes, respectively. Structurally - technological aspects of unijunction and multi-transition electrodes are considered in [1]. It should be noted, however, that all materials used are too expensive or do not provide long-term stability of electrochemical devices. For the first time, a device for the decomposition of water under the influence of sunlight in photo-cells was demonstrated in the works of Fujishima and Honda [2].

![Figure 1. Schematics of water electrolysis with semiconductor and metal electrodes: a) p-type, b) n-type.](image)

The photo-electrolysis schematics using semiconductor electrodes of p- or n-type conductivity are shown in figure 1 a, b, respectively. A quantum of light generates electron-hole pairs in a semiconductor electrode. The hole diffuses to the interface between the semiconductor and the aqueous electrolyte, and the water molecule is oxidized there. Electrons pass along the external circuit to a metal cathode, where hydrogen ions are reduced.

The main problem is the choice of material for photo-electrodes. It should be inexpensive and affordable, resistant to photo-corrosion. The most important characteristic for a semiconductor photo-electrode is the width of the forbidden band and its position relative to the electrochemical potentials of water oxidation and hydrogen reduction [2, 3]. The values of the band gap should be in the range from 1.7 to 3 eV (figure 2). These parameters are determined by the fact that the photo-electrode must create a potential sufficient for the electrolysis of water and at the same time efficiently absorb and transform light into electricity in the widest possible wavelength range. In comparison with the binding energy of water molecules ($E_{c.b} = 1.23$ eV), mono-crystalline silicon is characterized by a narrower width of the forbidden band ($E_g = 1.1$ eV). For this reason, silicon has not been used for a long time as a material for photo-electrodes and its application in photolysis has not been practically considered [3]. Further development of the field of application of silicon is associated with the development of various composite materials based on it. One of the most known and easily obtainable composites is porous silicon (pSi).
Porous silicon was discovered at the beginning of the second half of the last century. Since then, a large volume of scientific research has been carried out both in methods of obtaining and studying properties and in the variety of practical use of the unique properties of this promising nano-composite material [4-8]. The most significant characteristic of pSi for photo-electrolysis, as noted above, is the band gap (Eg pSi). According to the results of studies by different authors, Eg pSi is essentially dependent on porosity.

When the porosity is increased from 5% to 95%, the width of the forbidden band varies from 1.1 eV, which in practice corresponds to single crystal silicon (c-Si), to Eg PC = 3.05 eV [9], which can correspond to a porous crystalline (PC) with characteristic pore wall sizes less than Units of nanometers. In addition, a material with such porosity has an extremely large surface area, which can reach 1000 m$^2$/cm$^3$ [4]. Thus, nano-porous silicon is a very attractive option for use as a material for photo-electrodes [9, 10].

An important limitation for the practical application of nano-porous structures is the extreme fragility of the material. If the Young's modulus is 160 GPa for c-Si, then in a PC with a porosity of 90% this value decreases to 0.87 GPa [4]. This does not allow the use of nano-porous silicon in the form of free membranes or electrodes. Therefore, to support nano-porous films it is necessary to use special support elements. As a carrier of the nano-porous layer, it is proposed to use gradient-porous silicon structures. The first gradient-porous structures (GPSi), in the form of free membranes, are described in [11]. The developed technology of deep anodic etching makes it possible to form macro-porous membranes with thickness from 150 μm to 550 μm. Such membranes were used as electrodes for micro-fuel elements [4, 12]. The strength of porous membranes was ensured by the successive formation of layers with different morphologies of macro-pores as shown in figure 3a, b, and c. In contrast to the hetero porous crystalline (HPC) structures with several spatially separated layers, the GPSi-var structures are characterized by a smoother change in pore morphology in the depth of the porous layer (figure 3d). In the present experiment, the GPSi-var structures were fabricated by the method of deep anodic etching of p-type silicon wafers with a resistivity of 10 Ω cm.
The structures were formed on plates with the orientation of the surface of the plates (111) and (100). The thickness of the porous film (figure 4) was 320 μm. The etching was carried out at a constant current density of 2.5 mA / cm² in a solution of hydrofluoric acid in alcohol HF: C₂H₅OH: CTAC = 200: 50: 1 (CTAC-cetyltrimethylammonium chloride). The etching time was 480 minutes. In contrast to GPSi-2 and GPSi-3, the production mode of GPSi-var structures does not provide a change in the electrolyte during the etching process. Spontaneous formation of the morphology of the porous structure occurs at a constant density of the anodic etching current [13].

The porous surface, in comparison with the surface of the original silicon wafer, acquires a brilliant black color (black Si). However, there is no significant increase in the roughness of the porous surface, which is typically characteristic of the porous surface of single-layered or multilayer macro-porous films. This is due to the fact that a nano-porous layer is located on the surface of the macro-porous layer (figure 4b, c, d). This layer is formed during the process of disproportionation occurring during the anode etching regimes used. The thickness of the nano-porous layer in the structures depicted in figure 4c, d is between 0.2 and 3 μm. A similar structure was observed in the etching of silicon wafers with a different orientation of the initial surface. As shown in [13], a nano-porous film is formed on the surface at the initial stages of anodic etching and is retained throughout the etching process. To obtain porous membranes after the anodic etching process was completed, the remaining un-etched portion of the silicon wafer on the bottom of the pores was removed by mechanical polishing.

An essential characteristic of the surface of photo-electrodes is the ability of absorption over a wide range of frequencies and angles of the incident light. Reflectance spectra obtained from the surfaces were studied in Ref. [14]. Figure 5 shows the comparative reflection spectra, the front side (marked in the figure as "shiny side") and the back side of the membrane (marked in the figure as "matte side").
The analysis of the obtained spectra indicates, first of all, that in the considered wavelength range, the reflection of light is at least an order of magnitude lower than on the surface of the original silicon wafers. It should be noted that the roughness of the surface of the initial surface of the silicon wafers was $R_z = 16.56 \text{ nm}$, and for the nano-porous region this value was $R_z = 30.3 \text{ nm}$. In addition, we noted a weak dependence of the reflection coefficient on the angle of incidence of light on the nano-porous area of the electrode. At the same time, the reflection coefficient strongly depended on the angle of incidence for the original silicon. As follows from the dependencies shown in figure 5, the presence of the nano-porous layer on the surface of the macro-porous layer (front, shining side) compared to the mechanically polished macro-porous side provides higher antireflection characteristics.

4. Water splitting method

Figure 6 shows the experimental design, which will confirm the operation of a single-layer porous silicon electrode. The structure is a Pt-H$_2$O-por-Si / p-Si system. The counter electrode (4) is a platinum wire, and the sample itself is opposite (2). The contact is made to the back side by the liquid method. In the center of the bulb (1) is a gas outlet. The experiment was conducted under two conditions when illuminated with light and in the dark, and its reaction to light was also tested (figure 6). The voltage in the absence of light was about 40 mV, with a light supply of -65 mV. The current was 1.2 $\mu$A and 1.8 $\mu$A, respectively. The working area in this experiment is about 0.5 cm$^2$. There is an interesting feature that with a completely darkened sample, a current of the order of 0.8 $\mu$A. The flowing current has sufficiently low values, which corresponds to a slow flow of the decomposition reaction of water. Therefore, it is necessary to reduce the resistance of the sample, because it is about 30 kOhm. The main contribution to this value is made by the porous film [10].
5. Conclusions
In the work it is proposed to use the GPSi structures as photo-electrodes for devices of artificially photosynthetic hydrogen. The results of the investigation of the physicochemical properties of HPC-var silicon structures indicate the greatest attraction of the use of such structures based on silicon for the photoelectric decomposition of water. The use of GPSi structures allows to reduce the reflection coefficient below the level of 0.1%, and also extend the range of use of the light range of wavelengths. Photo-electrodes based on HPC structures significantly reduce the dependence of the magnitude of the generated photocurrent on the angle of incidence of light. Further optimization of the structural and technological design of photo-electrodes based on HPC-var silicon structures and, in particular, reduction of the series resistance of the electrode is necessary.

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