

Solar Elements on the Base of Low-dimensional Composite Structures

Sergii Khrypko, Valery Kidalov

Abstract— *Converting solar energy into electrical energy with using photocells is a major task for developers and research groups. Production of solar batteries passed through some steps, taking into account technical and economic aspects which was associated with improvement of their parameters.*

This way the first generation solar batteries are based on substrates of silicon single crystal (Si). Continuous research to reduce the costs of their production and increase the efficiency of solar batteries led to the development of solar modules which having a conversion efficiency of solar energy 12-16%. Using of polycrystalline silicon and other silicon shapes allowed reduced the cost of modules, but due to the efficiency of solar energy conversion.

Solar batteries of the second generation were based on thin films of amorphous silicon. Using this technology allows reaching the coefficient of performance (COP) solar battery is about 12% with a significant reduction of costs.

Solar batteries which based on the third generation established crystals and nanoporous materials. Developed photocells by nano-enabled technologies to make them more effective through the use of nanoscale clusters of semiconductors that have optoelectronic properties that are changed by quantum physical effects. In addition, the absorption bands can be optimally adapted to the wavelength of incident light. Three-dimensional grids of quantum dots is technologically possible. These solar structures can lead to increased efficiency of solar energy conversion more than 15%, which could double the existing practical efficiency of solar batteries.

Index Terms— *Clusters, Composite structures, Nanotechnology, Porous silicon, Solar cell.*

I. INTRODUCTION

One of the promising trends in modern semiconductor technology is the use of low-temperature electrochemical processes in realizing basic organisation the operations of the technological cycle of production of semiconductor devices and integrated microcircuits. Today mostly used electrochemical polishing, etching, deposition of films and so on. Improved anodic oxidation methods that allow production

dielectric film for masking and surface passivation and electrochemical doping of semiconductors.

Nano-technology in combined with surface science, provide significant potential to contribute to sustainable energy systems, which let to more efficient use of existing energy sources that can qualitatively new solutions towards new sources and energy systems. This creates a lot of attention in the creation of such systems not only in academic circles, but also among investors, governments and industry. The motivation for the use of nanostructured materials for solar batteries is to develop nanotechnology. There is a need to use nanostructured surfaces light harvesting or antibacterial materials. Nano-porous materials such as porous silicon and nanocomposite structures play an important role in converting solar energy [1-4], [7] and [8], and the etching of semiconductors plays a major role in the production of micro- and nano-porous clusters [5], [6].

Of particular interest to researchers is the possibility of obtaining in way low-temperature electrochemical treatment promising new kinds of semiconductor materials, particularly porous silicon.

The porous silicon obtained by method etching silicon in solutions of hydrofluoric acid is formed in a matrix in a controlled network of cavities (pores) of different morphology, size and orientation. The resulting silicon nanocrystals are characterized by some specific and unique properties. Thus, developed adjustable surface of porous silicon makes it promising for manufacturing super sensitive gas, liquid sensors, etc.

The use of porous silicon in combination with established its surface oxides SiO_2 and thin top oxide can solve such actual technological problems as the formation of thick dielectric films, deep doped layers and the wide films which widely used as a transparent ohmic electrodes in solar batteries, and also allows you to make efficient gettering unwanted impurities in the functioning actual instrument layers.

Found that nanocrystalline silicon is a photoluminescence in part of the visible range of light. So on this basis, unlike single-crystal silicon can be created optoelectronic instruments different purposes: photodetectors, emitters, LEDs, displays and more.

The aim of our work is to create on based a porous silicon device structures, namely - photoconverter elements for solar batteries and research their characteristics to study physical phenomena and processes that occur in them.

II. THE POROUS SILICON

Porous silicon is one of form of the chemical element Si, which contains nanoporous clusters in its microstructure, which makes large ratio surface to volume. It was discovered

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Sergii Khrypko, Institute of management, Classic Private University, Zaporozhye, Ukraine,

Kidalov Valery, Sciences Institute Nanotechnologies, Berdyansk State Pedagogical University, Berdyansk, Ukraine,

in 1990 and formed on crystalline silicon wafers using electrochemical etching. Porous silicon has photoluminescence and electroluminescence. [9]

First of all we were interested in identifying the impact of geometric and structural parameters of nanocrystals on the features of electronic and phonon excitations in nanostructures and their optical properties, as well as the establishment of regularity and clarify the mechanisms, which responsible for radiation nanocrystals on various stages of structural transformation.

It is known that the morphology of porous silicon affects a number of factors. To them can to be include conductivity type monocrystalline silicon, crystallographic orientation plates, resistivity, dopant type, light regime (the wavelength of light used, light intensity, duration), current density, time of the process of anodizing, the electrolyte composition and etc. It was necessary at first experimentally and theoretically investigate the mechanisms of growth and formation of silicon nanocrystals in during electrochemical dissolution of the surface in the process of obtaining and subsequent thermal treatments.

Creating a porous silicon structures with a fairly wide range of values of the characteristic parameters made possible through the use of different methods for their preparation.

For electrochemical etching of silicon and efficient temperature control of the electrolyte, continuous recovery his concentration near to the surface of the silicon sample and control of topographic features surface of porous silicon, we have developed and manufactured the installation setting, and the scheme is shown in slide 1.

During digestion electrolyte becomes turbulent near to a fixed plate that provides: 1) controllability and uniformity of the temperature of the electrolyte, 2) renewal of electrolyte in related plate layers, 3) anti-lock bubbles of hydrogen sample surface, 4) the availability of the influence torque setting electrolyte morphology porous material. (Fig. 1)

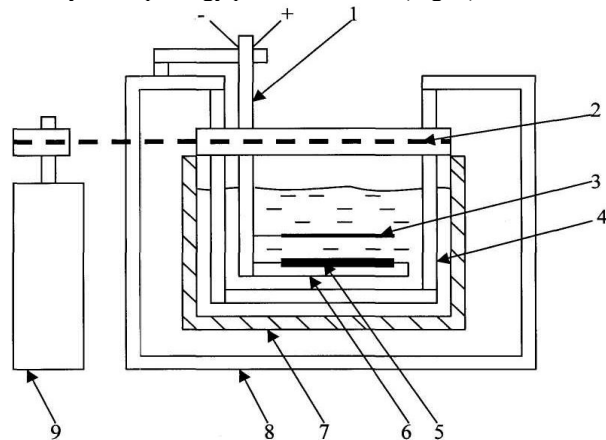


Fig.1. View on electrochemical etching of silicon: 1- holder, 2- Belting, 3 – Pt wire, 4 – rotary electrochemical bath, 5 – silicon, 6- holder of silicon, 7 – thermostat, 8 – hull, 9 - engine

Multiple reflection incident on the front surface of the solar element radiation with a view to more effective use and management of reflective and absorbent material characteristics, which was achieved by way of obtaining films of porous silicon by method of electrical anodizing in solution.

Electrochemical etching the surface of silicon samples was carried out in a special device in galvanostatic mode in the electrolyte with different ratios of HF: H₂O: C₂H₅OH = 2: 1: 1. current density of anodizing was 50 mA / cm², and the duration of anodizing - from 3 to 14 sec.

Was used 48% hydrofluoric acid and 96% alcohol. Cathode served platinum wire diameter of 0.3 mm. The thickness of the porous silicon layer was 130 nm. Porosity silicon samples was about 50%.

After anodized samples were washed with deionized water, blown flow of hot nitrogen and kept in the dark.

The morphology of porous silicon after anodizing shown in Fig. 2.

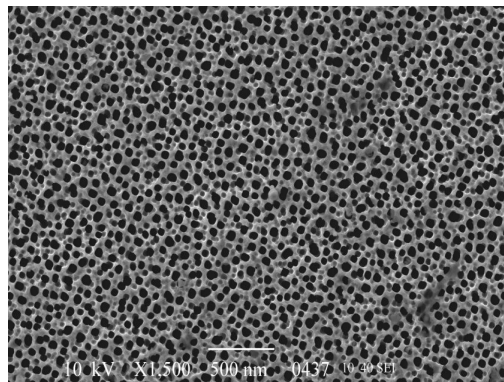


Fig. 2. The morphology of porous silicon after anodizing

Formation of porous films on the surface Si leads to improved conversion efficiency of solar cells made on base of them. This improvement leads to more than on 25% [10, 11, 12].

III. CHARACTERISTICS OF METAL DEPOSITION ON SILICON

One of the effective ways to increase factor of useful activity photoconverter is the use of wide-gap semiconductors, for example thin leading of oxide (TLO) In₂O₃, SnO₂, ZnO, which have value band gap (E_g) of 2,0-3,7eB. [13, 14, 15].

The metal precipitated on Si has some characterized features. Silicon and precipitated metal is usually show weak interaction, which leads to the growth of 3D islands on the mechanism Folmer-Weber.

Their use is due to the fairly large transparency (> 80%) in the visible wavelength range, significant refractive index (n ≈ 1,6-2,3), sufficiently low surface resistance values (R_{surface} ≈ 10-70 Om/cm²), a variety of low temperature technological methods of production (T ≈ 390-970K).

Parameters process of making films SnO₂:F erected in Table 1

PARAMETERS	THE OPTIMAL VALUE
Interval from nozzle to silicon	380mm
Diameter of nozzle	0,3mm
Carrier gas	air
Pressure of gas	2 kg/cm ²
Speed flow solution	8 ml/min
Temperature on holder of silicon	300 ⁰ C-550 ⁰ C

Preparation of the solution for the manufacture of thin films SnO₂:F performed by dissolving 2,3 g SnCl₄·5H₂O in 5 ml 2M HCl. Dissolution took place in a mixture of 20 ml of

ethanol. As a source of fluoride was used ammonium fluoride (NH_4F), which was added to the solution in certain proportions (F:Sn, wt.%): from 5 wt.% to 25 wt.%. Before the spraying process, solution was heated to 90°C during 15 minutes. Film $\text{SnO}_2\text{:F}$ precipitated by method of spray pyrolysis with temperature 460°C and had a thickness of 600 nm.

For practical application films preferably reach the optimal values of transmittance and electroconductivity, which calculating with help of criteria for quality (figure of merit): $F_{\text{TS}} = T^{10} / R_{\text{surf}}$, where T - pass the respective wave length; R_{surf} - surface resistance.

Spray pyrolysis system is housed in a closet with forced exhaust ventilation. (Fig. 3)

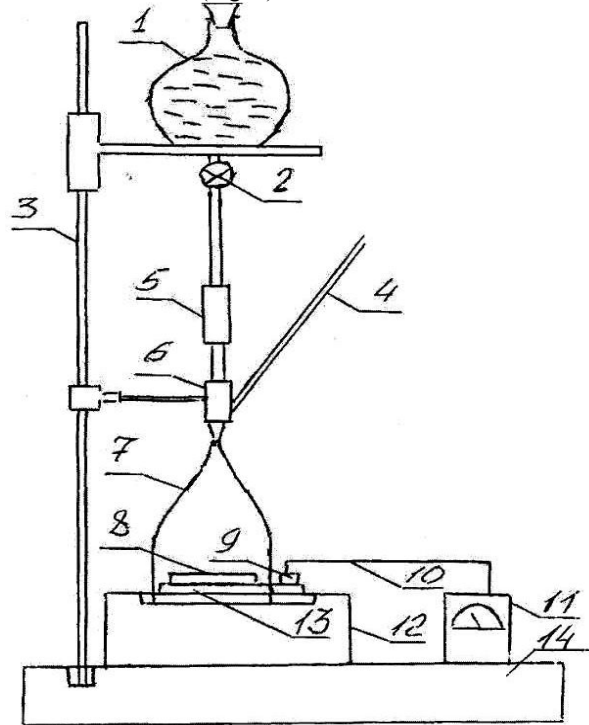


Fig.3. View on system spray pyrolysis (TLO):

1 – solution in flask; 2 – faucet; 3 – tripod; 4 – pipe to the compressor; 5 – flowmeter; 6 – aerograph; 7 – camera; 8 – substrate; 9 – silicon; 10 – thermocouple; 11 – thermometer; 12 – heater; 13 – holder of silicon, 14 – footing.

The temperature of the process is given insulated heater (12) round shape with a diameter of 160 mm, which is powered by a laboratory transformer and by which regulated voltage in an electrical circuit and gradually changing the temperature of the heater (12). At the same heater are lining holder (13) with the substrate (8), which made the application of film and plate-satellite (9) attached Cr-Al thermocouple (10). The temperature is controlled by a digital meter temperature (11) precision 1°C . The solution is fed from the flask (1) through the pipe system with regulator (2) and flowmeter (5) to aerograph (6), by which to regulate the flow of solution and air. The design aerograph attachment (6) let to move and rotate him. Air inflated from compressor on the pipeline (4). Camera (7) is made of quartz glass and has a specific shape: round bottom, and the top has cone narrowing. This form of the top of the camera (7) eliminates compression spray torch (Fig.4).

In accordance with computations and experiments identified the following dimensions of main camera $\alpha = 30^\circ - 35^\circ$, $a = 90 - 110$ mm, $b = 48 - 69$ mm. Camera (7) located on four guide rods, mounted in the support (14). Thus formed air exchange with the outside space.

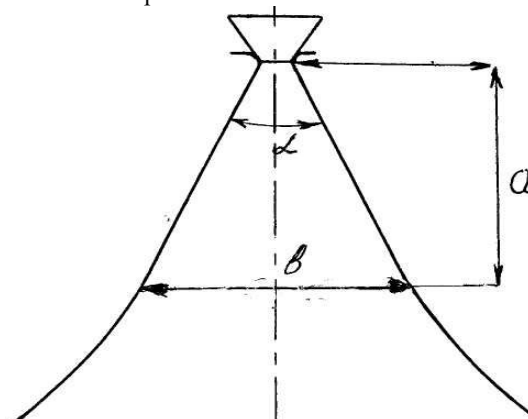


Fig.4. Element construction connection of nozzle and camera (7) with aerograph (6)

Researching of electrical properties of films $\text{SnO}_2\text{:F}$, obtained by method of spray pyrolysis, showed the following results.

The value of surface resistivity and specific resistance decreases monotonically with increasing concentrations of fluoride in the initial solution. Minimum value of surface resistance $R_{\text{surf}} = 1.85 \text{ Om/cm}^2$ and resistivity $\rho = 2,40 \text{ Om}\cdot\text{cm}$ are achieved when the concentration of $N_{\text{F}} = 17$ wt.% and a temperature of the substrate surface $t = 460^\circ\text{C}$. Further increase in the concentration of N_{F} results to the growing of the resistance films (Fig. 5, 6).

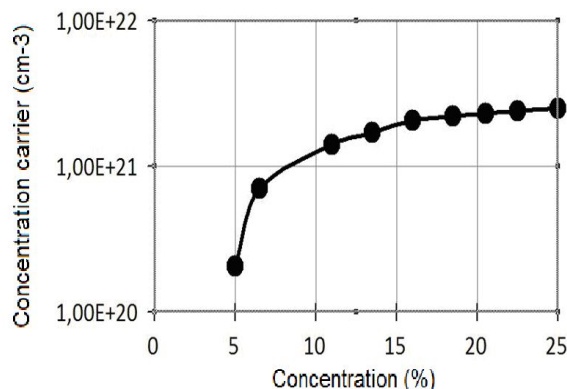


Fig.5. Dependencies concentration carrier of fluoride from concentration at deposition: temperature - 460°C and film thickness $\text{SnO}_2\text{:F} - 600$ nm.

Growth content of fluoride ions in the solution causes the falling value of the resistance films to certain values because as anions F in the lattice $\text{SnO}_2\text{:F}$ displaces anions O^{2-} that promote made of additional quantity of free carriers – electrons. Further increase in the concentration of $N_{\text{F}} > 17$ vah.% can to be due to reaching the solubility of fluorine tin dioxide lattice. The excess fluorine atoms are not fixed in units of lattice SnO_2 and therefore do not lead to the formation of additional electrons, but rather increase disordering lattice, creating local levels capture of carriers, which leading to increased resistance values. The growth in concentration carrier charger with the concentration of the alloying

component in the solution at the substrate 460°C also leads to decrease of their Hall's mobility. [16]

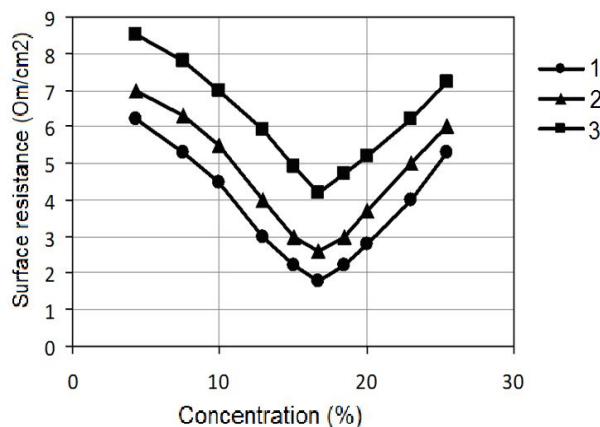


Fig.6. Dependencies surface resistance from concentration carrier of fluoride with thickness films $\text{SnO}_2\text{:F}$ - 600 nm for different temperature deposition: 1 - 460°C , 2 - 500°C , 3 - 380°C .

Research transmission and reflection spectra of films $\text{SnO}_2\text{:F}$, manufactured with different concentrations of fluoride in the substrate temperature 460°C showed that with increasing bandwidth fluorine content increases and reaches a maximum value in the wavelength range 700-1100 nm. Thus, when the fluoride concentration 15% transmittance is 82%, and at 25% - 88%. Reduced transmission in the infrared range, in our opinion, may be associated with increased levels doped films of fluorine. At wavelengths of 500-1000 nm film $\text{SnO}_2\text{:F}$ have a better reflection than film with fluoride concentrations of 5%, but the wavelengths of 1500 nm, the reflection is minimal (20%) for films with a fluoride concentration of 5%.

Thus, the demonstrated possibility of producing thin films of $\text{SnO}_2\text{:F}$ using the technology of spray - pyrolysis alcohol-water solution based SnCl_4 . The resulting film thickness of 600 nm are sufficiently satisfactory electro-mentioned parameters: surface resistance - 1.85 Ohm/cm^2 , specific resistivity - $2.4 \text{ Ohm}\cdot\text{cm}$, the mobility of carrier - $37 \text{ cm}^2/(\text{V}\cdot\text{s})$, the concentration of carrier - $5\cdot 10^{21} \text{ cm}^{-3}$, optical transmission - 85%.

IV. CREATING A SOLAR ELEMENTS

Was created the technological route of manufacturing solar elements, which providing high bandwidth of radiation, internal reflection and maximum generation of charge carriers. [17, 18, 19]

For the manufacture of solar elements were used single-crystal silicon wafer grown by Czochralski method and doped with boron, n - type electroconductivity, specific resistivity of $2 \text{ Ohm}\cdot\text{cm}$ thickness of 300 microns and crystallographic orientation of the surface (100) and a diameter of 76 mm.

Chemical treatment of plates carried out in peroxide - acid ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:5$) and peroxide - ammonia ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:5$) mixtures. Then the plates washed in deionized water and dried in a centrifuge. n+ emitter created on the front surface using single-stage diffusion of phosphorus at a temperature 850°C system in single-band diffusion of systems. As the dopant used POCl_3 . The

thickness of the n+ layer was 0.3 microns, and surface resistance - 20 Ohm/cm^2 .

Contact grid on the front surface and a solid film on the back surface of the silicon sample thickness of 1 micron created by magnetron sputtering of aluminum installation "Oratorio-2M" at a pressure of $7 \cdot 10^{-5} \text{ Pa}$ followed by annealing of temperature 550°C for 15 minutes. After spraying was using photolithography. Then the plate was cut by using of skrayber samples area of 1 cm^2 .

Measurement current-voltage characteristic (CVC) solar elements was carried out under conditions of power light 1000 W/m^2 and a temperature of 18°C . Energy conversion efficiency (ECE) solar elements efficiency reached 17.1%. (Fig.7).

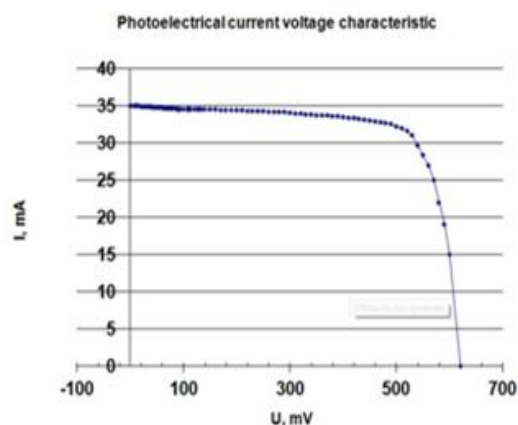


Fig.7. CVC solar cell

CONCLUSION

Retrieved an ECE, which amounted to 17.1% of the solar elements on porous silicon. As used anti beating covering wide-gap semiconductors SnO_2 doped fluorine.

In our opinion some improvement options can be explained by an increase in active surface area plane of the porous silicon, which reduces the loss of light on the boundary air - crystal and limits the generation of additional photocarrier in porous silicon because of more width of prohibited zone than in the monocrystalline silicon

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