# FORMATION AND APPLICATION OF BLACK POROUS SILICON FOR RENEWABLE ENERGY

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**Abstract.** Sunlight is the most abundant source of potential energy on the planet. It is important to note that while the usage of solar energy increases significantly in the world, the prices prominently decrease. Using performed black porous silicon , it is possible to produce even cheaper solar cells with higher efficiency, that is important today.
In this work the current state of photovoltaic (PV) and crystalline silicon usage was overviewed, and the application producing by three different methods and optical properties of black silicon samples were presented and discussed.

**Keywords:** photovoltaic, solar cells, black silicon, optical properties.

## Introduction

Sunlight is the most abundant source of potential energy on the planet, which usage is increasing annually in the world [1] and in Lithuania [2], respectively. The installed PV base in 2015 has been roughly 20% residential rooftops, 20% commercial buildings like hotels and malls, and 60% utility plants connected to the grid [3]. If harnessed properly, sunlight could easily exceed current and future electricity demand [4]. The creating of solar power by converting sunlight into electricity could reduce the consumption of fossil fuel and emissions of $CO_2$ to atmosphere.

Every second the Sun emits 3,826 eW to the space. Every hour enough energy from the sun reaches the Earth to meet the world's energy usage for an entire year. People living in northern countries (such as Lithuania and Latvia) may think that the solar energy is not effective in winter time. In summer time the solar power stations actually generate more energy, yet in the cold period of the year, generation of clean energy is also effective. The power stations work even better in the winter time as solar cells work more effectively at low temperature. In 2020 Lithuania's intends to reach solar PV capacity of 3 W of power for one inhabitant (in total 10MW for the entire country). However, in 2011 the average of PV energy produced in Europe was 102 W/1 person. In 2016 in Germany it was 304 W/1 person [5].

The analysis of energy market of the last ten years shows the decrease of approximately four times in price of photovoltaic energy in the world. [1, 6]. Bloomberg New Energy Finance predicts (Fig. 1), that the prices of photovoltaic energy (PV) in the world will decrese, and in 2025 the PV energy will cost less in comparison to other types of energy [7]. It is due to the decrease in price of silicon wafers up to 70%, approximately up to 60% of solar cells, 50% of modules as estimated in the last decade [3].

Figure 2 shows the development of the solar cells efficiency of different element types during the period of two decades. The II-V multi-junction concentrator solar cells are on the top in terms of efficiency, but actually they are very expensive in today's market [1]. With a global market share of about 90%, crystalline

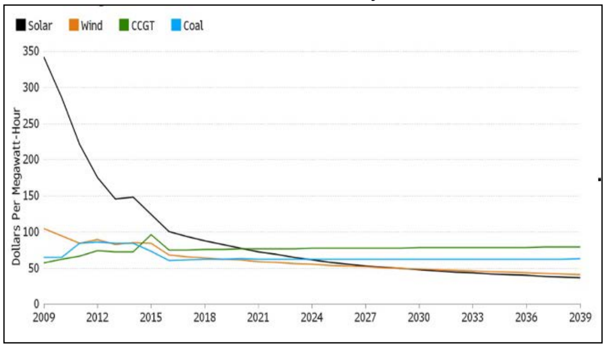



*Figure 1. Reality and forecasts of the PV energy prices in the world from 2009 to 2039 (from 2009 to 2016 is actual situation is depicted) [7]*

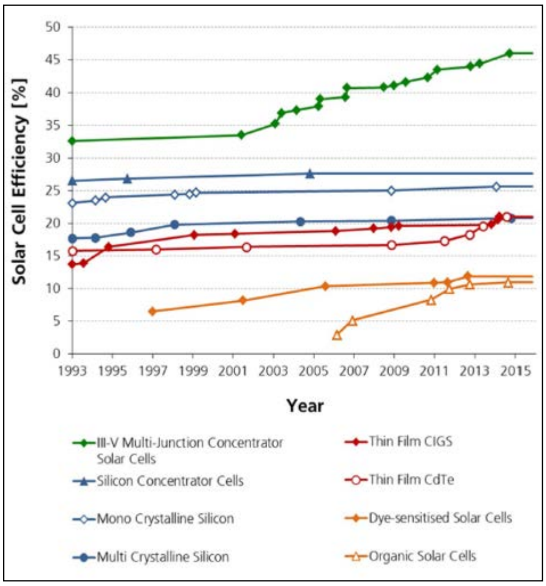



*Figure 2. Development of solar cells efficiency [1]*

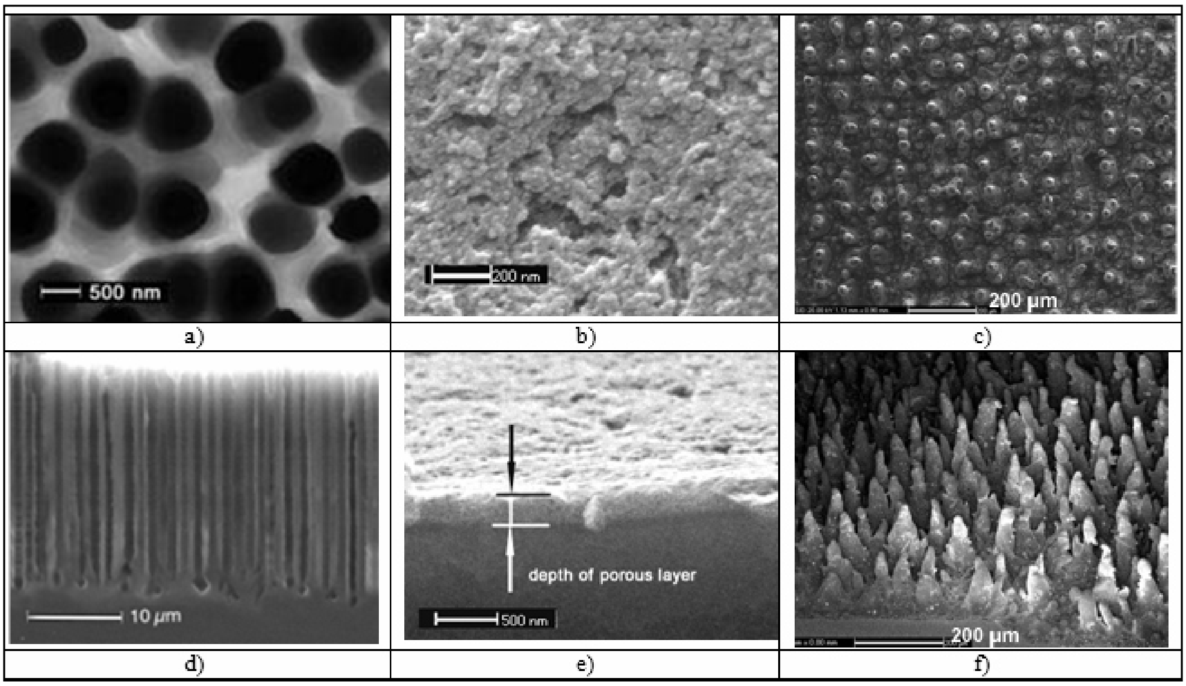



*Figure 3. The SEM view from the top and from the side of black porous silicon, produced using electrochemical etching (a, d), chemical etching (b, e) and ablation by lazer (c, f) method*

silicon is by far the most important photovoltaic technology today [8].

Solar cells on the background of crystalline silicon can be produced using different methods, such as reactive ion etching (RIE) [9, 10], ablation with femtosecondary laser [9, 11], electrochemical [9, 12] and chemical etching [9, 13]. Using performed black porous silicon, it is possible to produce even cheaper solar cells with higher efficiency, that is cost-effective today.

This paper presents production and overview of three methods of black porous silicon formation such as electrochemical etching, chemical etching and texturisation of surface using He-Ne laser. The optical properties such as reflection and photoluminescence of black porous silicon samples (BPS) were measured and presented.

## Experiment

In this work black porous silicon was performed on the n-type (100) oriented silicon (resistivity 1-1.5 Ωcm) wafers. The firs type of black porous silicon samples were made using electrochemical etching equipment. The deep pairs were generated by illuminating the back side of the sample with a 50 W halogen lamp (range of wavelength 380-750 nm), through a circular window in the electrochemical etching tank. PS layers were prepared in HF solution using ultrasonically enhanced (frequency 22 kHz, US power density 1.16 mW/cm$^2$) DC electrochemical etching. Time allocated for etching was 5 and 7 minutes, respectively. The porous silicon samples were produced at 105 mA/cm$^2$ current density.

For black porous silicon chemical formation hydrogen fluoride (HF, 50%), vanadium pentoxide ($V_2O_5$, Fisher certified grade), silver nitrate ($AgNO_3$), deionized water and nitric acid ($HNO_3$) were used. Silicon was etched for 10 and 60 seconds.

The microcones on the surface of cristallyne silicon were produced by ablation of He-Ne laser ($\lambda$ =1064 nm, $\tau$ = 150 ms, $\upsilon$=12.5 Hz, P = 1.0 MW), when influence angle was set 90°. As catalyst nickel ($d_{Ni}$=100 nm) was used. For formation of black silicon layer, the number of laser impulses was chosen like 1600 and 2000

To carry out a morphological analysis of the samples, Scanning electron microscope (SEM) Apollo Cam Scan 300 (30 kV, resolution 1.5 nm) was used.

The absorption of black silicon samples was investigated by Shimadzu spectrometer (within the range of 200 nm to1000 nm).

The photoluminescence analysis of samples was accomplished by FS900 Spectrofluorimeter System (Edinburg Analytical Instruments) in the visible range of light. The excitation source was a xenon lamp (450 W).

## Results and Discussions

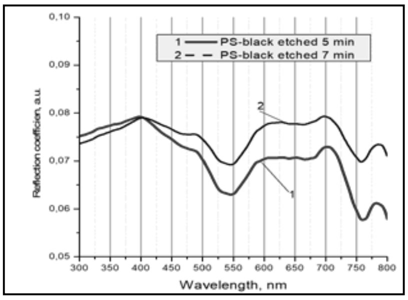
The electrochemically performed black porous silicon layers, using power density 1.16 mW/cm$^2$ of ultrasound excitation, were investigated by SEM (Fig. 3 a, d) and it was observed that the shape was more branched on the top for the pores that were etched for 7 minutes in comparison to the pores of BPS that were etched for 5 min. The width of pores has varied from 0,5 to 1,6 μm and the depth of pores 25 and 41 μm (corresponding to etching time) was determined.

After SEM investigation of chemically etched silicon (Fig 3 b, e), the depth of porous black silicon layer 280 nm and 500 nm was detected, when etching time 10 s, and 60 s was used.

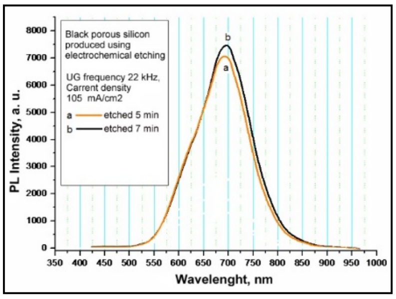
After performation of black silicon layer by laser ablation, the periodical structures of pyramids were detected and investigated. The size of pyramids has varied from 130-170 μm (Fig.3 c, f).

All produced samples by these three methods looked black. The comparison of optical properties (Fig. 4) of produced BPS layers demonstrates, that the lowest reflection of light had the BPS produced by electrochemical etching, especially in the range from 500 to 600 nm (Fig. 4 a). It depended on the surface morphology and layers porosity. The BPS performed chemically, showed lower reflection in the range from 350 to 650 nm (Fig. 4 b), and the reflection of both samples was very similar. The insignificant movement of curves can be explained by the depth and morphology change of porous silicon structures. The BPS produced by laser ablation demonstrated, that the reflection of samples substantially depended on the number of impulses and correlated with the number of impulses (2000) chosen (Fig. 4 c).

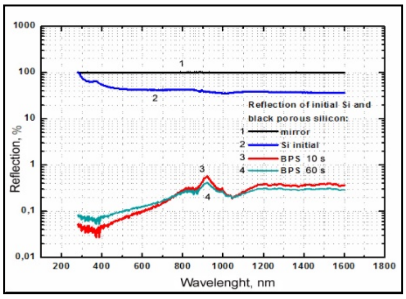
The photoluminescence (PL) measurements showed the movement of PL peaks depending on the performance method of the BPS layers. PL maxima of the samples produced by electrochemical etching (Fig. 4 d) were detected at the 685 and 700 nm, when the etching time of 5 and 7 min was used. Chemically produced samples showed the PL maxima at 664 and 670 nm (Fig. 4 e). The PL spectrum of black silicon layers, produced by He-Ne laser, moved significantly according to the range of short wavelength (Fig. 4 f) and the peak was detected at 430nm. The movement of photoluminescence shifts of spectrum from 700 nm to 430 nm in the electrochemically, chemically and by laser produced samples could be explained by the



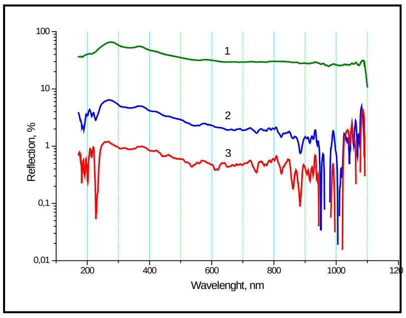

*a) reflection spectra of electrochemically etched BPS*



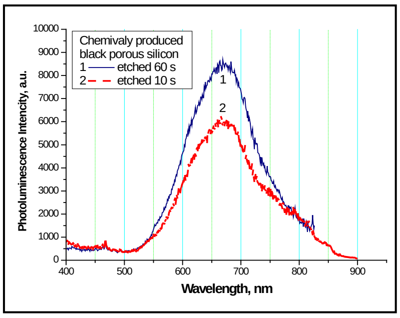

*b) reflection spectra of chemically etched BPS*



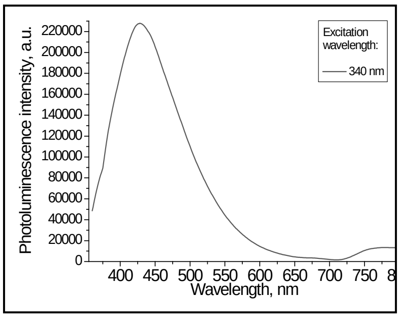

*c) reflection spectra of BPS produced by He-Ne laser*




*d) PL spectra of electrochemically etched BPS*




*e) PL spectra of BPS produced by chemical etching*




*f) PL spectra of BPS produced by He-Ne laser ablation*

*Fig. 4. The spectra of reflection and photoluminescence of black porous silicon layers*

change of surface states and concentration increase of recombination centres, which radiate energy of higher frequency.

The growth of photoluminescence intensity correlate with etching time and depend on the effective surface stretch of porous silicon layer, which define concentration of recombination centers on the surface.

The overview of optical properties of BPS shows the possibility to produce really black silicon using all mentioned formation methods. Comparison of the production time and equipment used for different formation methods presupposes that the laser ablation method for BPS formation is the most ecological method as well as the electrochemical and chemical etching. However, the production of one square centimetre by laser ablation takes about 15-20 minutes, and for formation process a special room is required. The formation of BPS by chemical and electrochemical etching on all surface of wafer can take only several minutes, whereas chemical etching does not require electricity and is cheaper. This feature is very important for the mass-production of solar cells.

## Conclusions

1. The black porous silicon, using three formation methods, was produced and the depth of structures for electrochemically etched silicon 25 and 41 µm, for chemically etched silicon 280 nm and 500 nm (corresponding to etching time) was detected and the high of pyramids 130-170 µm of black porous silicon layers, performed by laser ablation, was determined.

2. The produced black porous silicon by different methods shows a very low reflection of light (less than 1%) in UV/VIS range.

3. The photoluminescence intensity increased, when longer etching time was used. The growth of photoluminescence intensity depended on effective surface stretch of porous silicon layer, which defined concentration of recombination centres on the surface.

4. The movement of photoluminescence shifts of spectrum from 700 nm to 430 nm in the samples, produced by tree different methods, could be explained by the change of surface states and concentration increase of recombination canters, which radiate energy of higher frequency.

5. The comparison of different formation methods of black silicon structures presupposes, that ablation with laser is the most ecological method for formation, but the fastest and cheapest way for the production of solar cells is a chemical etching.

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