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Investigation of electrochemically produced black silicon with silver nanoparticles

Abstract. *Black silicon is new material, which first time was produced in 2006, using femtosecondary laser. Using electrochemically performed black silicon we can produce cheaper solar cells with higher efficiency, comparing to monocrystalline and polycrystalline silicon solar cells, what is important economically today. Efficiency of solar cells also can be increased by application of nanoparticles with inherent plasmon resonance properties. Black silicon with precipitated plasmonic nanoparticles (such as silver or gold) can revolutionary change the market of solar cells. In this work the black silicon were prepared electrochemically from n-type (100) silicon wafers at room temperature in HF:H_2O:C_2H_5OH solution by ratio 2:1:1, using ultrasound excitation of 4.4 mW. The silver nanoparticles were precipitated from silver nitrate and sodium citrate colloidal solution. The structures of black silicon and black silicon with silver nanoparticles were investigated by SEM and lower reflection coefficient of samples of black silicon with Ag nanoparticles was detected. The size of Ag nanoparticles has varied from 30 to 70 nm. Presence of silver on silicon surface was detected by SEM-EDX technology.*

Streszczenie. *Czarny krzem jest nowym materiałem, który został wyprodukowany po raz pierwszy w roku 2006 przy użyciu lasera femtosekundowego. Wykorzystując przetworzony elektrochemicznie czarny krzem można wyprodukować tańsze ogniwa słoneczne o wyższej sprawności w porównaniu do ogniw słonecznych z monokrystalicznego i polikrystalicznego krzemu, co jest obecnie ekonomicznie uzasadnione. Sprawność ogniw słonecznych może być również zwiększona poprzez zastosowanie nanocząstek o właściwościach rezonansu plazmowego. Czarny krzem z wytrąconymi nanocząstkami plazmowymi (takimi jak srebro lub złoto) może zmienić w sposób rewolucyjny rynek ogniw słonecznych. W niniejszej pracy czarny krzem przygotowano elektrochemicznie wykorzystując struktury krzemowe typu n (100) w temperaturze pokojowej w roztworze HF:H_2O:C_2H_5OH o proporcjach 2:1:1, wykorzystując pobudzanie ultradźwiękowe o mocy 4,4 mW. Nanocząstki srebra zostały wytrącone z roztworu koloidalnego azotanu srebra i cytrynianu sodu. Struktury czarnego krzemu i czarnego krzemu z nanocząstkami srebra zostały przebadane poprzez SEM, w wyniku czego stwierdzono niższy współczynnik odbicia próbek czarnego krzemu z nanocząstkami Ag. Rozmiar nanocząstek Ag zmieniał się od 30 do 70 nm. Obecność srebra na powierzchni krzemu została stwierdzona za pomocą technologii SEM-EDX. (**Badania wytworzonego elektrochemicznie czarnego krzemu z nanocząstkami srebra**).*

Keywords: black silicon, silver nanoparticles, plasmon resonance, electrochemical etching.
Słowa kluczowe: czarny krzem, nanocząsteczki srebra, rezonans plazmonowy, wytrawianie elektrochemiczne.

Introduction

Nowadays, it becomes more and more important to develop new alternative energy technologies because of exhaustion of fossil fuels resources. Solar energy is the most promising renewable energy source, which can be transformed into electricity or heat by many different types of solar energy technologies based on monocrystalline or polycrystalline silicon. It should be noted that current production of solar cells is dominated by crystalline silicon modules because of well developed fabrication techniques and relatively high efficiency; either, due to low reflectance coefficient of porous silicon (less than 15% of incident light is reflected back, which greatly induces the conversion efficiency of photovoltaic devices), because light trapping is an important property of increasing the efficiency of silicon-based solar cells [1].

Black silicon (BS) is a type of porous silicon (PS), which first time was performed using femtosecondary laser [2, 3]. Nowadays, PS and BS can be produced by using reactive ion etching (RIE) [4], electrochemical [5] and chemical etching [6] methods and application of electrochemically produced BS to solar cells technology gives an opportunity to produce solar cells with higher efficiency, what is important economically today.

But still, there are some issues with thin film solar cells. Because of small thickness of the film absorbance of sunlight is reduced because of many energetic losses (reflection of interfaces at the surface of a module and carrier, photovoltaic effect and insufficient energy in the form of infrared light) [7]. Another way to increase solar-energy conversion is through surface plasmons, i.e., collective surface oscillations of conducting electrons in metal nanostructures that tend to trap optical waves near their surface [8]. Noble metals like silver and gold are ideal for this purpose, because they can scatter visible light very efficiently and create a trapped mode for the incident light at the metal dielectric interface [9, 10]. By combining BS and nanoparticles (NPs) with plasmonic properties gives a great possibility to increase the efficiency of silicon solar cells by reduction of light reflectance through BS and increase of light absorbance through plasmonic NPs.

In this work the black silicon was prepared by electrochemical etching method and silver NPs with plasmonic properties were precipitated to its surface in order to improve optical properties of BS.

Experimental

The BS samples were made by electrochemical etching method. The deep pores were generated by illuminating the back side of the sample with a 50 W halogen lamp (wavelength range: 380-750 nm) through a circular window in the electrochemical etching tank. The distance from the sample to lamp was 40 cm. The contact on the back side of silicon was made from InGa alloy and was fastened by an aluminum ring to make contact only on the periphery of wafer. The cathode was made from stainless steel. For electrochemical etching n-type (100) oriented silicon (resistivity 1-1.5 Ωcm) was used. BS layers were prepared in HF solution using ultrasonically enhanced (frequency 22 kHz, power density 1.16 mW/cm^2) DC electrochemical etching. Etching time varied from 3 to 20 min (current density: 105 mA/cm^2). Silver nanoparticles were precipitated from silver nitrate ($AgNO_3$) and trisodium citrate ($Na_3C_6H_5O_7$) colloidal solution by application of 50 µl of it to BS surface and kept for 30 seconds in ultrasound bath.

The surface morphology and cross-section of BS samples, pores parameters, Ag NPs size and distribution on BS surface were investigated and evaluated by scanning electron microscope (SEM) Apollo Cam Scan 300 and

ImageJ software [11]. Chemical analysis was made by energy dispersive x-ray spectrometer (EDX).

Optical properties of BS samples were investigated by UV/VIS spectrometer "Avantes AvaSpec-2048" UV/VIS/NIR spectrometer at room temperature in wavelength range 300-800 nm" in the range from 300 to 800 nm. Spectrometer is based on AvaBench-75 symmetrical Czerny-Turner construction with 2048 pixel CCD detector.

Results and discussions

BS layers electrochemically etched by ultrasound excitation with power density 1.16 mW/cm^2 were investigated by SEM. After etching the BS samples had three different layers: 1-initial (irregular), 2- intermediate layer with unformed structure, 3 – layer with regular pores [12]. Excitation by ultrasound produced stronger process of cavitations in BS, which helped to detach first irregular layer. It was observed that the shape of pores was more branched on the surface of BS etched for 7 minutes (Fig. 1c), comparing with the pores on surface of BS that was etched for 5 min (Fig. 1a).

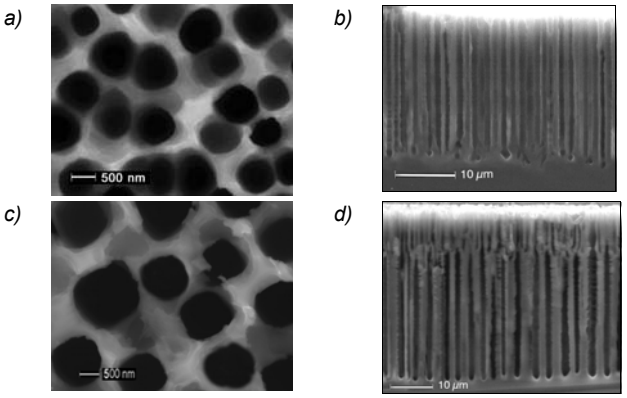

Fig.1. SEM micrographs of electrochemically etched BS: a) surface of BS etched for 5 min, b) cross-section of BS etched for 5 min, c) surface of BS etched for 7 min, d) cross-section of BS etched for 7 min

Parameters of pores of BS wafers were evaluated with ImageJ software and are presented in table 1. As it is seen from table 1, with the increase of etching time the diameter of pores increase gradually, while the depth of pores doubles with increase of etching time for 2-3 min.

Statistical evaluation of pores parameters versus etching time lets us choose etching conditions in order to obtain variable pores parameters and to control the depth of pores corresponding to unprocessed silicon wafers thickness.

Table 1. Pores parameters of BS wafers vs. etching time

Etching time, min	Medium width of pores, µm	Medium depth of pores, µm	Porosity, %
3	1.34 ± 0.35	10 ± 4	34 ± 2
5	1.64 ± 0.32	25 ± 2	39 ± 2
7	1,81 ± 0.28	41 ± 2	43 ± 2
10	1.96 ± 0.21	70 ± 2	49 ± 3
13	2.10 ± 0.14	83 ± 3	56 ± 2
15	2.27 ± 0.23	92 ± 4	67 ± 3
20	2.43 ± 0.14	98 ± 5	72 ± 3

After electrochemical etching the Ag NPs were precipitated on BS surface. In Fig. 2 SEM micrographs of BS samples with precipitated Ag NPs are shown. As it is seen from Figs 2a and 2b distribution of spherical Ag NPs on the BS surface is hardly visible, because that the size of pores is 10-15 times greater than the size of Ag NPs. From Fig. 2c it is visible, that the size of Ag NPs, ununiformly distributed on the surface of BS, varies from 30 to 70 nm. Distribution of Ag NPs inside of pores in BS layers is shown in Fig. 2d.

From SEM analysis it was observed, that Ag NPs are distributed not only on the surface of BS, but inside of pores, which can be very useful in solar cells technology, by guiding the scattered light by Ag NPs from surface and pores to contact group, herewith, enhancing the energy output.

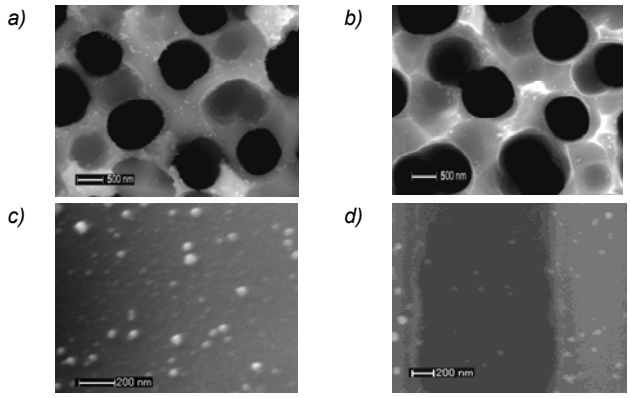

Fig.2. SEM micrographs of electrochemically etched BS with Ag NPs: a) Ag NPs distribution on BS surface etched for 5 min, b) Ag NPs distribution on BS surface etched for 7 min, c) Ag NPs distribution on BS surface, d) Ag NPs distribution inside of BS pores

Table 2. EDX quantitative results of BS layer with precipitated Ag NPs

Element	Weight, %	Atomic, %
C K	10.09	18.93
O K	19.68	27.70
Si K	65.24	52.33
Ag L	4.99	1.04
Total	100.00	

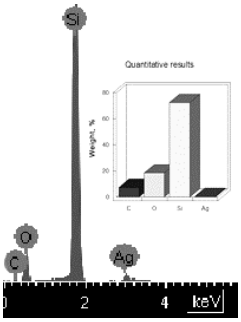

Fig. 3. Chemical analysis of BS layer with precipitated Ag NPs made by EDX

The presence of Ag NPs on BS surface was additionally proved by EDX analysis. The results of EDX investigation of BS layers with precipitated Ag NPs are presented in table 2 and Fig. 3. From table 2 it is seen, that Ag on Si surface amounts only 5% from total percentage weight and was detected at 3 keV (Fig. 3). The same position of Ag peak was found by Zeng F. and other authors [13].

In Fig. 4. the map of Ag NPs distribution on BS surface is shown. From Fig. 4 it can be seen, that Ag NPs distribution on Si surface is not uniform. This may be caused by position of BS layer in ultrasound bath and distribution of Ag NPs in colloidal solution.

Optical properties of BS layers were analyzed at room temperature by UV-VIS spectrometer. Reflectance spectra of investigated BS samples are shown in Fig. 5. As it seen from graph below, reflectance of BS wafers (curves (1) and (2)) is less than 10%, which let us assume, that porous silicon produced in this work can be classified as black

silicon. Similar results were found by other authors [14, 15] in the same wavelength range.

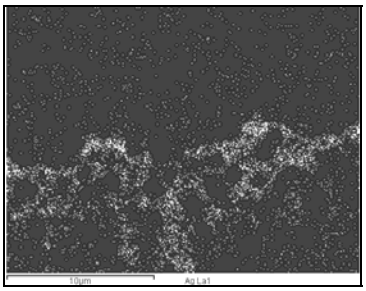

Fig. 4. Map of silver nanoparticles on porous silicon surface

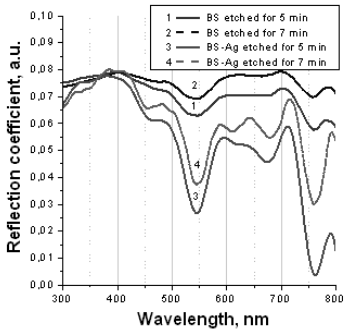

Fig. 5. Reflection coefficient of BS etched at 5 and 7 min and with Ag nanoparticles correspondingly

After precipitation of the Ag NPs to BS surface, reflectance of modified BS wafers twice decreased (curves (3) and (4)) in the range from 400 to 800 nm. Two minimums of effective reflection coefficient were found at 547 nm and 760 nm and in BS sample etched for 5 min. Reflection coefficients were 0.027 a.u. and 0.003 a.u. correspondingly. Obtained results show that samples modified with Ag NPs better absorb sunlight, especially in near infrared region, comparing with unmodified etched samples. Effective decrease in reflection coefficient at 547 nm gives better light absorption and good compatibility with ITO layer, which usually have higher reflectance of green light.

Conclusions

The black silicon in this work was produced by electrochemical etching method and modified with Ag NPs precipitated to BS surface from colloidal solution in ultrasound bath. SEM analysis of BS wafers has revealed the formation of round-shaped pores with different width and depth parameters. Statistical analysis of pores parameters have shown that the depth and width of pores can be controlled by selecting appropriate etching time.

SEM analysis of BS samples with precipitated Ag NPs have shown ununiform distribution of Ag NPs on the surface of BS wafers. Ag NPs were also observed inside of pores in BS layer. It was evaluated that the average size of Ag NPs varied from 30 to 70 nm. The presence of Ag NPs was additionally prooved by EDX analysis, which showed that the quantity of Ag in BS samples amounts almost 5% from total percentage weight.

Analysis of optical properties in wavelength range from 300 to 800 nm has revealed very low reflection coefficients in BS samples modified by Ag NPs and it was proved that, the use of plasmonic Ag NPs on BS surface can effectively decrease reflection of samples in wavelength range from 400 to 800 nm, especially at 547 nm and in near infrared region.

In conclusion, we can state, that BS wafers with precipitated Ag NPs produced in this work distinguish unique optical properties with very low reflectance values can be used in solar energy technologies, SERS spectroscopy and other sensorial applications.

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