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POROUS SURFACE SILICON LAYERS IN SILICON SOLAR CELLS

POWIERZCHNIOWE WARSTWY KRZEMU POROWATEGO W ZASTOSOWANIU DO KRZEMOWYCH OGNIW SŁONECZNYCH

The porous silicon (PSi) layers have been studied in the aspect of their application in the multicrystalline silicon (mc-Si) solar cells. The macroporous layers were prepared by double-step chemical etching prior to the donor diffusion. They have been investigated using scanning (SEM) and transmission (TEM) electron microscopy to reveal the morphology of PSi layers. The techniques of spectral response and current-voltage characteristics have been used to determine the opto-electrical parameters of the solar cells. The porosity was measured by the mercury porosimetry and nitrogen sorption method. The porous layers reported here have had a sponge-like homogeneous structure over the whole 25 cm^2 surface of each sample and the decreased effective reflectance (R_{eff}) below 10%. As a final result the mc-Si solar cells with PSi layer were obtained with the conversion efficiency (E_{ff}) over 13%.

Keywords: silicon solar cell, porous silicon, surface texture

W pracy przedstawiono metodę uzyskania redukcji odbicia efektywnego (E_{eff}) poniżej 10% od powierzchni krzemu multikrystalicznego (mc-Si) dla promieniowania w zakresie 400 ÷ 1100 nm długości fali. Metoda polega na chemicznym trawieniu powierzchni mc-Si w roztworach na bazie HNO_3:HF i wytworzeniu powierzchniowej tekstury geometrycznej w formie porów o średnicy od 30 ÷ 800 nm i porównywalnej głębokości. Krzem multikrystaliczny z warstwami krzemu porowatego wykorzystano do wytworzenia ogniw słonecznych. W zależności od wielkości porów otrzymano ogniwa o sprawności konwersji fotowoltaicznej od 9.8% do 13.0%.

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1. Introduction

The global production of solar cells continues its phenomenal growth, reaching the level of 744 MWp in 2003 year. The mono- and multicrystalline (mc-Si) silicon as a basic material dominate the photovoltaic sector sharing 26.94% and 61.79%, respectively [1]. The advanced technology of multicrystalline silicon solar cells requires such surface structures, which enable the reduction of effective front reflection from 34.8% to less then 10% in the range of 400 — 1100 nm electromagnetic radiation, without antireflection coating (ARC) [2]. Industrial applications need, first of all, high output with a low cost, which eliminates many les effective techniques (see Tab. 1) [3].

TABLE 1

The methods applied for surface texturization for mc-Si. The R_{eff} values are in the range of 400 — 1100 nm

Method	R_{eff}	Type of surface texture	Technical description
Chemical etching in KOH or NaOH solution with photolithographic pattern	~ 20%	Regular inverted pyramids	Low throughput
Mechanical V-grooving Multi-wire sawing	~ 5%	Regular pyramids or grooves	Low throughput Low yield for fragile mc-Si
Laser texturization Laser scribing	~ 10%	Regular pyramids or grooves	Low throughput High cost High precision
Wet acid etching	~ 9%	Porous layer - sponge like structure Random pits	High throughput Difficulties with nucleation and control of the process
Electrochemical anodisation in HF + organic solvent	~ 10%	Porous layer	Low throughput
Reactive ion etching (RIE)	~ 3%	Random needle- to pyramid-like structures	Problems with optimization of the emitter formation and phosphorous silica glass etching
Reactive ion etching + KOH etching	~ 21%	Random needle-like pyramids	Problems with surface passivation quality
Reactive ion etching + etching in HNO_3:HF	~ 25%	Random needle-like pyramids	Problems with damaged emitter region
Chemical etching in KOH or	~ 24%	Random pyramids but mostly different geometric shape	Dependence on grain orientation
Chemical etching in HNO_3 - HF solution with photolithographic pattern	~ 3%	Regular honeycomb texture	Low throughput

2. Experimental

The substrates used in this work were "as-cut", p-type, 1 Ωcm mc-Si "Baysix" silicon wafers. Experimental solar cells were fabricated on the basis of the screen-printing technique used at the IMMS PAS [4]. The process sequence can be presented in the following steps: 1) saw damage etching and texturization, 2) the PSi layer formation in a "C1" solution consisting of 2HF(40%); $1HNO_3$ (65%); $2H_2O$; $2H_2O_2$; $1C_2H_5OH$ (vol.) for 20 min., 3) modification of PSi layer in another "C2" solution of 2HF; $98HNO_3$ (vol.) in the time range from 0 to 300 s, 4) the formation of n^+-p junction by phosphorous diffusion technique, 5) removal of the phosphorous silica glass (PSG), 6) the passivation by the thermal oxidation, 7) ARC TiO_x spray-on deposition, 8) the screen-printing of contacts, 9) firing in IR furnace.

The total reflectivity $R(\lambda)$ of the samples as a function of the wavelength was measured using a Perkin–Elmer Lambda-9 spectrophotometer equipped with an integrating sphere. The effective reflectivity was calculated from eq. (1):

$$R_{eff} = \int_{400}^{1100} R(\lambda)N_{ph}(\lambda)d\lambda \ / \int_{400}^{1100} N_{ph}(\lambda)d\lambda, \qquad (1)$$

where, $N_{ph}(\lambda)$ is the photon flux of the solar spectrum under AM 1.5 condition. The SEM and transmission electron microscopy (TEM) were used for surface structure investigation. Additionally, the porosity of the layers were investigated by mercury porosimetry, (a Carlo Erba — Porosimeter 2000), and by the nitrogen sorption method (an ASAP 2010). The external quantum efficiency (EQE) and current-voltage (I-V) characteristics were measured for the electrical characterization of mc-Si solar cells of different surface texturization.

3. Results and discussion

From the SEM and TEM observations of the cross-sections of the porous layer, the pore diameters were found to be comparable to their depth. The structure of the pores was independent of the grains orientation. It seemed that the size of pores had been controlled by the etching time in the C2 solution which can be observed in Fig. 1. The summarized results of the optical, structural and electrical analysis of the samples are presented in Tab. 2.

It is visible from Fig. 2, that the shape of pores is cylindrical and the PSi layer can be classified as a macropore. The arrow in Fig. 2 a) indicates about 100 nm-thick wall between two pores, which has degenerated high donor doped dose after diffusion process. This region limits the quantum and photoconversion efficiency of the solar cell with the PSi layer especially in the range of 400 — 600 nm [5].

The presented porous layer decreases the reflectance of mc-Si surface but as can be seen in Tab. 2 for samples a, b and c, the surface extension and, related to it, the

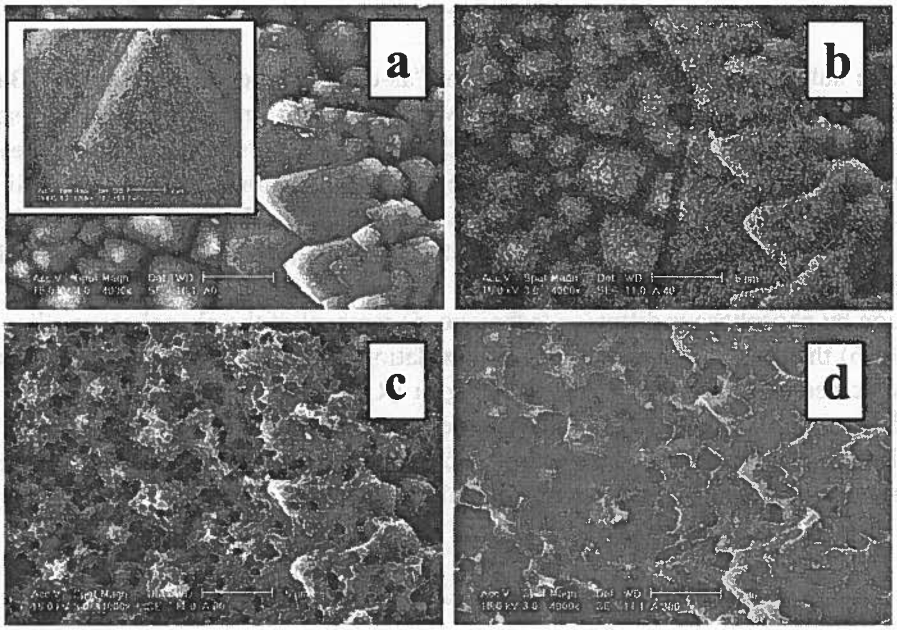

Fig. 1. SEM pictures of the mc-Si textured in KOH with PSi layer etched in C1 solution (a), and after etching in C2 solution for 40 s (b), 90 s (c) and 300 s (d)

TABLE 2
Physical properties and opto-electrical parameters of mc-Si solar cells with PSi. The data for mc-Si only after KOH etching are given for comparison

PSi stucture (Fig. 1)	Process technology	R_{eff} PSi [%]	R_{eff} solar cell [%]	Average size of the pores [nm]	Surface extension por./flat	Average EQE in 400-600 nm [%]	E_{ff} solar cell [%]
a	C1	9.3	3.81	~ 30	~ 50	32.8	9.81
b	C1 + 40 s in C2	12.6	3.67	~ 200	~ 29	44.3	11.25
c	C1 + 90 s in C2	17.1	3.24	~ 500	~ 23	46.1	11.75
d	C1 + 300 s in C2	21.1	5.19	~ 800	~ 18	60.8	13.02
mc-Si	after KOH	24.8	9.14	without pores	1.2 ÷ 1.3	59.3	12.15

average size of the pores and walls between them degrade electrical properties of the solar cell. The thickness of the walls between pores should be two times larger than p-n junction depth to avoid creation of degenerated region and to reduce the recombination process. However, it has been shown that the double-step chemical etching of 1 $\Omega \cdot$ cm resistivity p-type mc-Si in HF-HNO_3 based solutions can be used to obtain pores with diameter about 30 nm up to about 800 nm, which form the surface texture. For the mc-Si solar cells with PSi modified for 300 s, the E_{ff} is about 13% which is better in comparison with the cell of only KOH texturized surface.

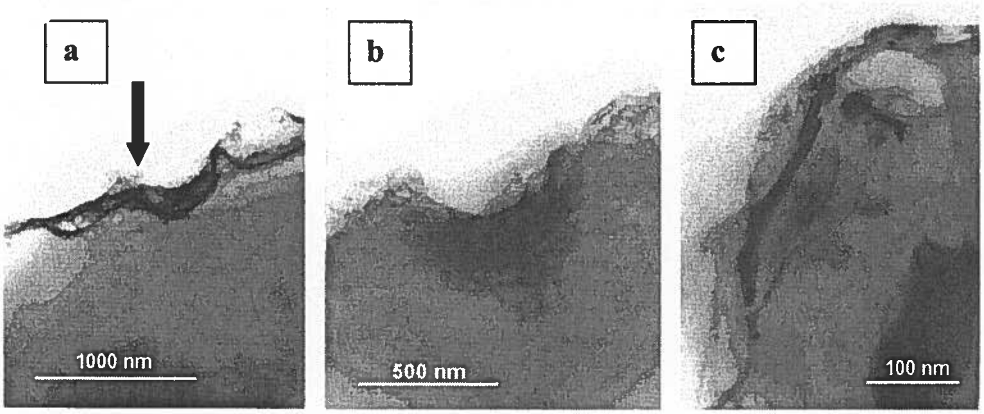

Fig. 2. Cross-section TEM images of mc-Si surface texture etched in C1 solution for 20 min. and in C2 for 300 s. Pore diameter and depth of 470 nm and 440 nm, respectively (a), 440 nm and 300 nm (b), 120 nm and about 150 nm (c)

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