

# Application of stain etched porous silicon in c-Si solar cells

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*In this work application of porous silicon (PS) to c-Si solar cells is presented. The PS layer is formed between the fingers of the Al grid contact by the method of stain etching. The short circuit current,  $I_{sc}$ , of the solar cells with PS between the grid contacts increases of 30–40% comparing with the solar cell without PS. The open circuit voltage decreases a little probably due to decreasing doping concentration of P in  $n^+$ -diffused layer, after stain etching, when 80 nm of it is converted to PS. The value of a fill factor does not change significantly. The spectral dependence of  $I_{sc}$  demonstrates that it increases in the whole spectral region. This could be related to a decrease in reflectivity and partially to an increase in transparency of the emitter after PS formation. The efficiency of solar cells increases of about 25–30%.*

**Keywords:** solar cells, porous silicon, stain etching.

## 1. Introduction

Soon after the report on photoluminescence (PL) from porous silicon (PS), the possibility for different applications of this material has been shown. Besides its application in light emitting diodes [1] it has been demonstrated that PS also exhibits photoconductivity and photovoltaic properties [2,3]. In the earlier PS applications to solar cells it was used as an emitter [2,3]. High values of PS resistivity, however, require application of a thin PS layer and optimisation of the contact grid to obtain higher value of the short circuit current. Another attempt is to apply porous silicon layers (PSLs) as an antireflective coating due to good antireflective properties of the reported PS [4].

In this work application of porous silicon to c-Si solar cells is presented. PS layer is formed by the method of stain etching between the fingers of the Al grid contact. This results in increase in short circuit current and in efficiency of  $n^+$ -p c-Si solar cell.

## 2. Experimental

Porous silicon layers were formed between the grid Al electrodes on the surface of  $n^+$ /p c-Si structures by the method of stain etching [4]. The P diffusion in p-type c-Si with  $11 \Omega \text{ cm}$  was performed to obtain  $0.5 \mu\text{m}$  diffusion layer with  $10^{19} \text{ cm}^{-3}$  P concentration. In the method proposed by us [4] the, so-called, "incubation time" of the stain etching reaction is excluded. The PSLs were obtained by the method of SE in  $\text{HF:HNO}_3:\text{H}_2\text{O} = 1:3:5$  solution. The proposed method of stain etching offers advantages of

a very simple technology that could be integrated with the solar cell fabrication process. Before etching process the front and back side of the c-Si wafer were covered with Al thin films ( $1500\text{--}2000 \text{ \AA}$ ) deposited by evaporation and annealed in vacuum ( $10^{-4} \text{ Pa}$ ) at  $450^\circ\text{C}$  for 15 minutes. Thin a-SiC:H film was deposited by magnetron sputtering through a grid mask over Al film before the stain etching. It was used as a protection of the Al contact below it during the SE process. As the prepared structure is subjected to stain etching, PSL is formed only between Al grid. Thus, Al grid directly contacts with  $n^+$ -diffusion layer of the Si solar cell and will collect the carriers generated by light. Al film on the back-side was used as an ohmic contact in solar cells. Etching was performed in a polypropylene beaker at room temperature under day light illumination. The beaker has an opening in the base that was clamped down to the front side of the silicon wafer by an o-ring. About 20 seconds after casting, the etching solution in the beaker, the Al film between the gride, covered by a-SiC:H, is dissolved. Change in colour (from grey through blue and yellow to violet) of the Si wafer and gas evolution were observed during formation of porous silicon. After etching the PSLs were rinsed in ethanol. An Al film was used as a back contact. The integrated reflectance of PSL was measured using a Perkin-Elmer UV VIS NIR dual beam spectrophotometer of 330 type with an integrating sphere. The IR measurements were performed on a Perkin-Elmer 1760X Fourier Transform spectrometer equipped with a vacuum chamber. The current voltage (I-V) characteristics of the solar cells were evaluated by a Keithley 236 source measure unit in dark and under light illumination of  $100 \text{ mW/cm}^2$ . The spectral dependence of the short circuit current was performed with a monochromator Digikrom 240.

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### 3. Result and discussion

Reflection electron diffraction patterns show presence of an amorphous phase on a surface of the obtained PSL IR transmission spectrum of the PSL sample (11  $\Omega$  cm, p-Si), obtained after correction for the substrate absorption is shown in Fig. 1. The spectrum exhibits characteristic absorption peaks at 2250, 1170, 1070, 880, and 840  $\text{cm}^{-1}$ , typical for different O-Si-H, Si-O vibrational modes. Additionally, in the region of the Si-H stretching vibrations, we observe only the 2250  $\text{cm}^{-1}$  band, assigned to O-Si-H stretching. Peaks related to the C-H vibrations at 2960, 2920, 2860, and 1470  $\text{cm}^{-1}$  are observed, too. The peak at 1720  $\text{cm}^{-1}$ , related to C = O vibrations, is presented as well. The presence of C-H and Si-O bonds is detected by SIMS and XPS analyses. We suppose that the origin of the carbon could be related mainly to absorption from the ambient air because stain-etched PSL, prepared without rinsing in alcohol, and PSL dry-etched in air also contain carbon, hydrocarbons, and carbonyl groups as we have reported in another paper [6].

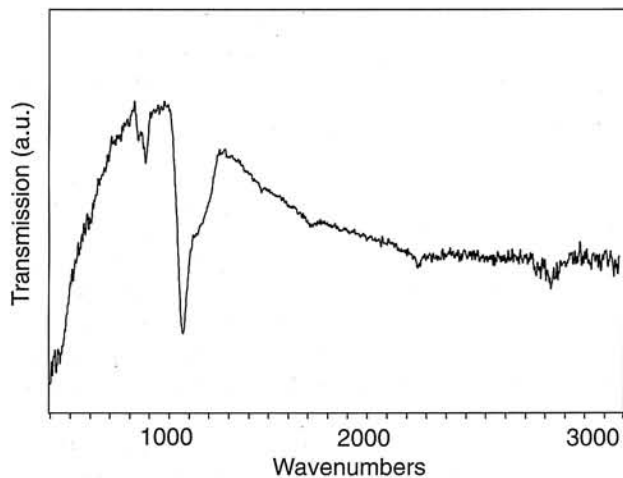


Fig. 1. IR transmission spectrum of a SE PSL sample (11  $\Omega$  cm, p-Si) obtained after correction for the substrate absorption.

As shown in Fig. 2, the integrated reflectance of a 1200 Å thick porous silicon film is lower than that of c-Si. That demonstrates that PSL could be used as anti-reflection coating, e.g., in Si solar cells, having in mind that its preparation is much simpler to implement and less expensive than multilayer AR coating which often requires deposition in vacuum.

The proposed PSL formation mechanism is based on previous studies of stain etching of Si [4]. Chemical etching of semiconductors can be considered as a localised electrochemical process. Microscopically local anode and local cathode sites form on the etched surface with local cell currents flowing between the sites during the etching. Therefore mechanism of chemical etching should incorporate the sources of excess holes and electrons in order to

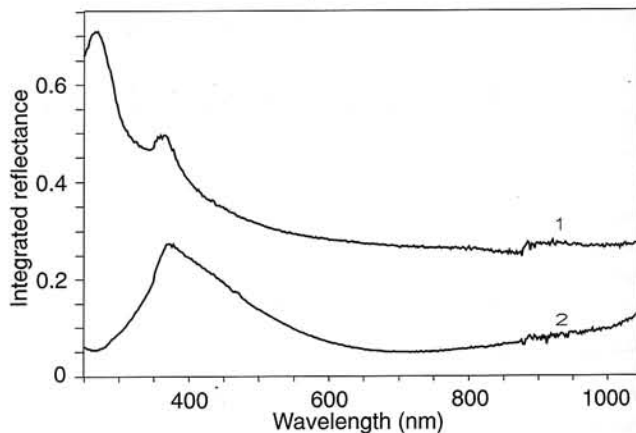
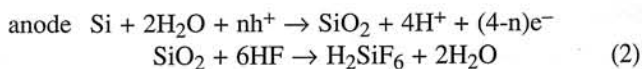


Fig. 2. Integrated reflectance of a 1200-Å thick SE porous silicon film (curve 1) and c-Si (curve 2).

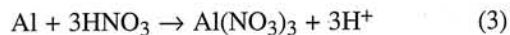
describe the charge transfer between electrodes. Reaction at the local anode is mainly Si dissolution. Reaction at the local cathode is a complicated reduction of  $\text{HNO}_3$  which causes holes to be injected into the Si. The proposed reaction at the local anode and local cathode sites are as follows



where  $n$  is the average number of holes required to dissociate one Si atom.

Sarathy [5] suggested that PS formation involved generation of  $\text{HNO}_2$  from  $\text{HNO}_3$  as a rate determining a step during the initial stages of the chemical reaction. They propose adding  $\text{NaNO}_2$  to sulfuric acid to evolve  $\text{NO}_2$  gas. This mixture is combined with HF to form etching solution which permits the PS formation without delay.

Another way to start the cathode reaction (2) is to generate  $\text{H}^+$ . Utilising the Al film deposited on the Si surface subjected to stain etching the following reaction is initiated



After dissolution of the Al and evolution of  $\text{H}^+$  (which occurs for 15–20 s) the cathode reaction (1) is started what provokes oxidation of Si.  $\text{SiO}_2$  subsequently reacts with HF to form water-soluble  $\text{H}_2\text{SiF}_6$  [according to Eq. (2)], hence Si is etched at the local anode. As a result PS films showing visible PL are prepared on the c-Si substrates with different type of doping and resistivity [4].

The I-V characteristics of the solar cells under illumination 100  $\text{mW}/\text{cm}^2$  are presented in Fig. 3. For comparison, the corresponding curve of the referent sample of conventional p-n<sup>+</sup> c-Si SC without PS is presented as well. The current density is not corrected for the contact area in spite of the fact that the Al grid finger size is not optimised for the sheet resistance of n<sup>+</sup> layer. The short circuit current,  $I_{\text{sc}}$ , increases of 30–40% in comparison with the SC with-

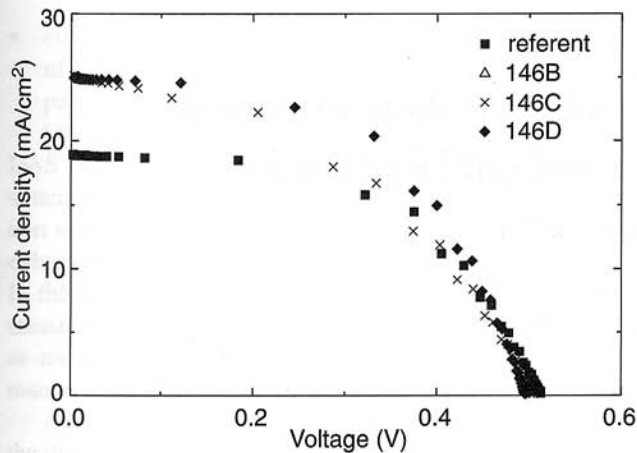


Fig.3. Current-voltage characteristics of c-Si solar cells with PS between the front grid electrodes. For comparison the corresponding curve for the referent sample without PS is shown, too.

out PS. The open circuit voltage decreases a little probably due to decreasing doping concentration of P in  $n^+$ -diffused layer after stain etching when 80 nm of it is converted to PS. The value of the fill factor does not change significantly. The efficiency increases of about 25–30%. As it can be seen from the spectral dependence of  $I_{sc}$  (Fig. 4) it increases in the whole spectral region. This could be related to a decrease in reflectivity [3,4] and partially to an increase in transparency of the emitter after PS formation.

#### 4. Conclusions

In this work application of the porous silicon to the c-Si solar cells is presented. The method of preparation of porous silicon layer by stain etching is proposed. It offers the advantages of a very simple technology that could be integrated with the solar cell fabrication process. Porous silicon layer is formed between Al grid contact. The lower reflectance was observed from the surface of the c-Si wafer when PSL are formed on it. This results in increase in the short circuit current and the efficiency of the in Si solar cells.

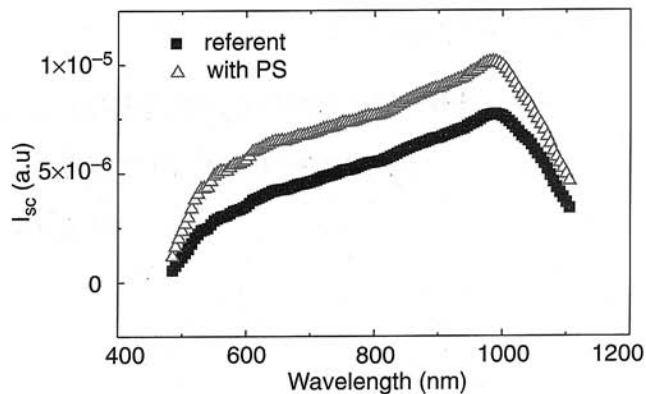


Fig. 4. Spectral dependence of the short circuit current of c-Si solar cell with PS between the front grid electrodes. For comparison the corresponding curve for the referent sample without PS is shown, too.

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