FIRST MULTICRYSTALLINE Si SOLAR CELLS WITH ELECTROCHEMICAL MACROPOROUS TEXTURISATION

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ABSTRACT: Electrochemical macropore formation is a cost-effective alternative technique for an improved texturisation of p-type multicrystalline silicon (mc-Si). This macroporous texturisation has the advantage over acidic chemical etching that the reaction is controlled by the applied current density and the results are easily reproducible. For the first time this method is applied to multicrystalline silicon. The texturisation can be done starting either from a polished or a saw damaged surface. In the latter case the saw damage removal and the texturisation are done simultaneously. The size (in the micrometer range) and the shape of the obtained structures can be varied by changing the reaction parameters. The optimisation of the macroporous surface results in a lowered effective reflectance for all grain orientations and an average value of 9-11 % for mc-Si POLIX wafers. First macroporous texturised mc-Si solar cells, obtained by the standard PHOTOWATT process without any modification of the cell process parameters, show excellent performance and a solar cell efficiency of 13.4 %.

Keywords: Multi-Crystalline - 1: Texturisation - 2: Porous Silicon - 3:

1. TEXTURISATION OF MULTICRYSTALLINE Si WAFERS

For improved solar cell efficiencies, the multicrystalline silicon (mc-Si) substrate has to be texturised. Anisotropic alkaline etching is still the most common industrial techniques used for Si solar cell production, as it allows high through-put processing at low cost per wafer. Due to the random orientation of the crystal grains, the average effective reflectance of the alkaline texturised mc-Si is still high (>20%).

Electrochemical oxidation of p-type Si in mixtures of hydrofluoric acid (HF) with specific organic solvents leads to the formation of macroporous layers [1-5], which can be very efficient in lowering the reflectivity on (100) oriented p-type c-Si [3-5]. An effective reflectivity of ~ 5 % was reached on (100) oriented, p-type Si with a resistivity of 10 Ω.cm [4]. Electrochemical macroporous texturisation has the advantage over chemical etching that the reaction can be controlled by the applied current density and that the results are easily reproduced. The thickness of the dissolved layer depends only on the applied current and the treatment time. For an efficient texturisation, a layer less than 5 µm thick is removed. An efficient texturisation will become more important as future Si solar cells will be thinner and will require efficient light trapping methods to maintain good absorption of the infrared light.

First p/n^+ junctions were realised on macroporous texturised, monocrystalline, (100) oriented p-type Si of 10 and 1 Ω.cm resistivity [6]. A reflectivity of 10 % and a solar cell efficiency of 12.6 % was obtained for the 1 Ω.cm wafers. Recently, we have been able to further improve the results for monocrystalline, medium doped, (100) oriented p-type Si, as well as to obtain macroporous texturisation on (111) oriented p-type Si. The results are presented in this paper.

The goal of this work is also to develop an efficient macroporous texturisation on 0.2-1.8 Ω.cm, p-type mc-Si. The texturisation can be done starting from a polished surface saw damaged surface. In the latter case the saw damage removal and the macroporous texturisation are done simultaneously. First mc-Si solar cells with macroporous texturisation, exhibiting a low reflectivity and an excellent performance, are obtained by a standard industrial process.

2. MACROPORE FORMATION ON MEDIUM DOPED, MONOCRYSTALLINE, P-TYPE Si

2.1 Experimental

To optimise the electrochemical conditions, a systematical study has been first undertaken on monocrystalline, mirror polished, p-type silicon wafer with a resistivity varying from 0.1 to 15 Ω.cm for (100) oriented samples and from 0.7 to 13 Ω.cm for (111) oriented samples. The nature of the organic solvent, the HF concentration, the time of the treatment and the current density were systematically varied. To remove the nanoporous layer, eventually formed simultaneously to the macropores, the samples were treated with 0.1 M KOH until the evolution of gas bubbles stopped. The galvanostatic Si dissolution was performed in a Teflon cell using a standard two-electrode set-up.

Scanning electron microscopy was performed using a Leica Stereoscan 440 microscope.

2.2. Results

We found out that macropores are formed on p-type c-Si in mixtures of HF with DMF and DMSO. The shape and size of the macropores obtained depend strongly on the reaction parameters. As an example, in Fig. 1 the influence of the HF concentration on the pore morphology is shown. The pore shape is square or round for low or high HF concentrations, respectively.

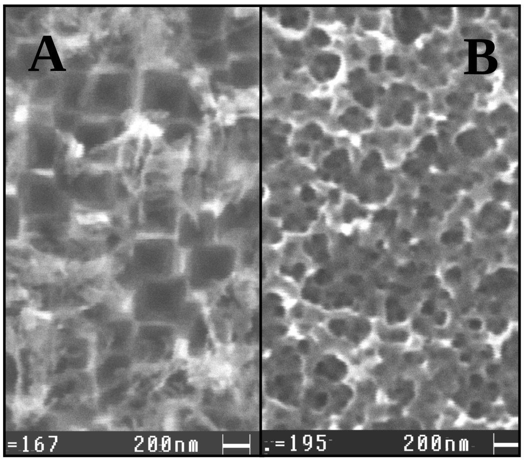

Figure 1: SEM images (plane view) of p-Si, (100) oriented, 0.2 Ω.cm, after passing a charge of 6 C/cm^2. A: 2 M HF/ DMF; B: 14.5 M HF/ DMF.

The macropores on 0.2 - 1 Ω.cm substrates proved to be too fragile for photovoltaic application (pore wall thickness around 50 nm) [7]. Therefore we chose the reaction parameters in a way that the pore walls get almost completely dissolved, resulting in micropyramids and square shaped etch pits for (100) oriented Si samples. The obtained morphology is similar to NaOH texturising, but the structures are smaller (around 1 µm). The angles are steeper and the resulting reflectivity is much lower. For (100) oriented c-Si samples we obtained an effective reflectivity (400 - 1100 nm) of 5.7 % (0.2 Ω.cm) and 5.3 % (1 Ω.cm) while for a NaOH texturised, (100) oriented c-Si sample, the effective reflectivity is around 12 %. P/n$^+$ junctions were fabricated on macroporous texturised (100) oriented c-Si samples of 1 Ω.cm. In spite of the simple process – no AR coating, no back surface field and no passivation, front and back contacts made by InGa alloy - a solar cell efficiency of 13.5 % (0.5 cm^2) was obtained.

For (111), 0.7 Ω.cm, p-type Si, an effective reflectivity (400 - 1100 nm) of 10.7 % was observed for the macroporous texturised surface using high HF concentrations, while the best results for (100) oriented wafers were obtained in low HF concentrations. As a conclusion, the reaction parameters have to be optimised for each material, as the result depends on crystal orientation and doping concentration.

3. MACROPOROUS TEXTURISATION ON MULTI-CRYSTALLINE Si

3.1. Experimental

The first part of the electrochemical experiments was performed to find an optimal structure for the texturisation of the mc-Si regarding the reflectivity. The mc-Si substrates used for this study had a resistivity in the range of 0.2 - 1.8 Ω.cm and were supplied by EUROSOLARE. The macropore formation was done in a mixture of concentrated HF with DMSO. The size and shape of the structures were investigated by Scanning Electron Microscopy (SEM).

3. 2. Surface morphology, reflectivity and transmission

The obtained structures are highly anisotrope, but nevertheless all grains of the sample are texturised. On (111) oriented grains, triangular etch pits are formed, while on (100) oriented grains the structure depends on the time of the treatment. During the first 10 minutes micropyramids develop, while after longer treatments square shaped etch pits are formed. Fig. 2 A and 2 B show SEM cross sections of two different oriented, macroporous texturised grains on 0.4 Ω.cm mc-Si (POLIX), starting from a chemically polished surface.

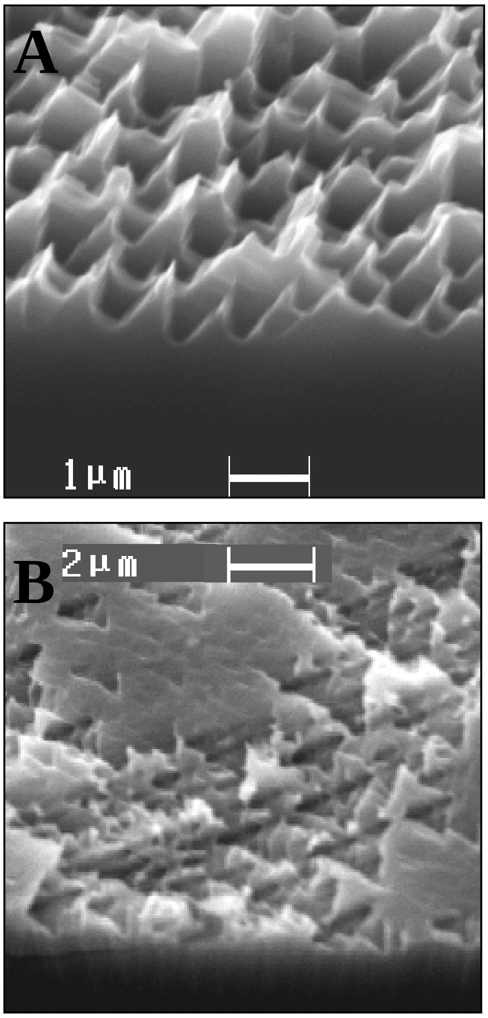

Figure 2: A and B: SEM images (45°) of the cross section of two different oriented grains on macroporous texturised mc-Si (POLIX), starting from a chemically polished surface.

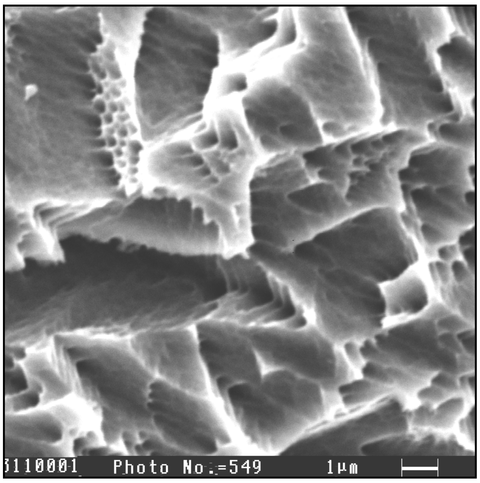

Figure 3: SEM images of macroporous texturised mc-Si (POLIX). Saw damage removal and texturisation were done simultaneously.

By varying the current density and the time of the treatment, it is possible to change the size of the structures. The results are well reproducible. When choosing the right reaction parameters (for example low HF concentration) no preferential etching of the defects is observed. Steps at the grain boundaries are below 5 µm. The texturisation can be done starting from a polished or a saw damaged surface. Fig. 3 shows the structure obtained when saw damage removal and texturisation are done simultaneously.

Fig. 4 shows several reflectivity spectra of macroporous texturised mc-Si (POLIX), starting from a chemically polished surface. Several reflection measurements were performed at different locations on the wafer in order to study the effect of the grain orientation.

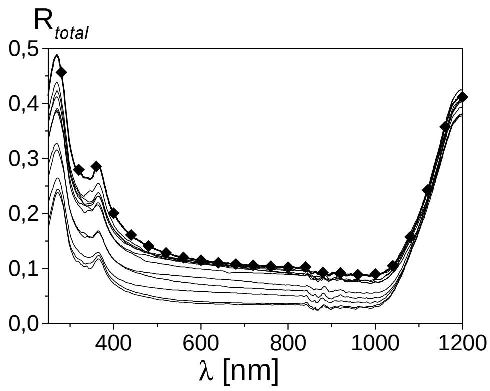

Figure 4: Reflectivity spectra of a macroporous texturised POLIX wafer (straight lines). For comparison the reflectivity curve of NaOH texturised, (100) oriented c-Si is also shown (◆).

The average effective reflectivity of the macroporous texturised mc-Si are 9.0 % when starting from a chemically polished surface and 11 % when saw damage removal and texturisation are done simultaneously (average of 10 samples each).
Fig. 5 shows the transmission spectra of macroporous texturised and chemically polished mc-Si . In the infrared region the transmission is significantly lowered in the case of the texturised sample because of an improved light trapping.

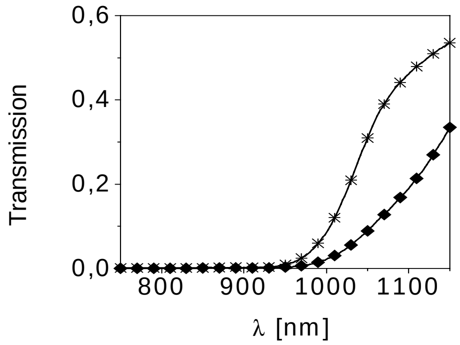

Figure 5: Transmission spectra of macroporous texturised (◆) and polished (✶) mc-Si (POLIX).

4.3. Solar cells

For solar cell processing we used chemically polished mc-Si wafers (POLIX, 10×10 cm^2) in which a 15 cm^2 area was texturised in the electrochemical double cell shown in Fig. 6.

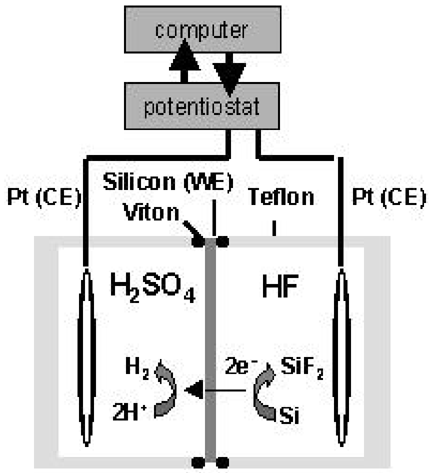

Figure 6: Schema of an electrochemical double cell with a liquid back contact. WE: working electrode; CE: counter electrodes.

The wafers were then processed in the standard production line of PHOTOWATT:

HF
↓
$POCl_3$ diffusion
↓
Plasma etching (opening of the junction)
↓
SiO_2
↓
TiO_2
↓
Screenprinting of contacts
↓
Annealing

After the processing the solar cell was laser cut in 5×5 cm^2 solar cells. Representative results of two texturised and a reference cells - processed in parallel and from consecutive wafers of the same ingot - are summarised in Table 1.

Table I: Performance of electrochemically texturised cells, and reference cell (standard process of PHOTOWATT, TiO_2 coating).

n°	treatment	V_{OC}/ mV	I_{SC}/ $mAcm^{-2}$	FF/ %	Eff./ %	R_S/ mΩ	R_{Sh}/ Ω
66c	polished	593	28.8	71.5	12.2	117	48
77c	texturised	598	30.0	74.3	13.3	96	89
88c	texturised	595	30.3	74.9	13.5	91	91

The comparison between texturised and reference solar cells shows that the short circuit current increases by around 5 %. The open circuit voltage is unchanged. The fill factor increases around 4 % due to a smaller serie resistance, which may be the result of a better contact. The shunt resistance slightly increases. An efficiency of 13.4 % compared to 12.2 % of the untreated samples is obtained. As only 60 % of the surface is texturised, it should be possible to obtain an efficiency of around 13.7 % once all the surface will be treated.

5. CONCLUSIONS AND OUTLOOK

The electrochemical formation of macropores is a promising method for the surface texturisation of mc-Si. The texturisation can be performed from a chemically polished surface as well as from a saw damaged surface. In both cases the resulting average effective reflectivity is around 10 %. An efficiency of 13.4 % compared to 12.2 % for the untreated samples is obtained for macroporous POLIX mc-Si solar cells fabricated with standard PHOTOWATT processing. The texturisation increases the short circuit current and the fill factor while the open circuit voltage is not affected. As only 60 % of the surface are texturised, the efficiency would reach 13.7 % once all the surface is treated. Further improvement is expected from optimisation of the process parameters. Finally, the combination of macroporous texturisation and a SiN_x AR coating may lead to high efficient mc-Si solar cells.

For industrial application, it seems desirable to perform saw damage removal and texturisation in one step. A new electrochemical cell is under construction, which will allow the treatment of frontside and backside of the Si wafer by a simple switch of potential over a 10×10 cm^2 area. Further work concerns the development of a multichamber cell for the simultaneous treatment of several wafers.

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