Influence of porous silicon formation on the performance of multi-crystalline silicon solar cells

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Abstract. The effect of formation of porous silicon on the performance of multi-crystalline silicon (mc-Si) solar cells is presented. Surface treatment of mc-Si solar cells was performed by electrochemical etching in HF-based solution. The effect of etching is viewed through scanning electron microscope (SEM) photographs that indicated the formation of a porous layer on the surface. Total reflection spectroscopy measurements on solar cells revealed reduced reflection after etching. In order to demonstrate the effect of this porous layer on the solar cell performance, illumination-dependent j - V characteristics and spectral response measurements were performed and analysed before and after etching. At all illumination intensities, short-circuit current density and open-circuit voltage values for the etched solar cell were higher than those before etching, whereas fill factor values were lower for the etched cell at high illumination intensities. An interpretation of these findings is presented.

Keywords. Porous silicon; solar cells; two-diode model; j - V characteristics.

1. Introduction

Porous silicon has a potential for various applications in sensing and photonic devices.^{1–5} The most widely applied features of porous silicon for solar cell applications include antireflection coating (ARC), surface texturing and surface passivation.^{6–9} Porous silicon thin films have relatively high optical absorption coefficient. Therefore, they can be used to reduce the reflection and improve the light absorption in the useful photovoltaic spectral range in multi-crystalline silicon (mc-Si) solar cells. The effectiveness of the porous layer as the antireflecting coating of the solar cell is confirmed.^{10–12} The porous silicon etch process has been implemented after junction formation and metallization. This approach can lead to selective emitter formation, proper surface reflectance and good electrical contact.¹³

In this paper the influence of porous silicon formation on the performance of mc-Si solar cells is presented. The porous silicon layer was formed selectively in the regions not covered by the grid, maintaining the front contact grid unchanged.

2. Experimental

The analysed cell was a 1.2 cm² partition of a cell denoted Q6-1380 (not encapsulated), which was thankfully provided by Q-Cells AG, Germany. Table 1 summarizes the cell properties taken from its datasheet.

The surface of the cell (top side) was anodized in an electrolytic solution of 44% HF and 99.99% ethanol in a

proportion of 1:1. The electrochemical etching cell was designed in single tank geometry.¹⁴ It consisted of two Teflon cylindrical sections, with a cavity in the upper section for electrolyte injection. A platinum electrode immersed in the electrolyte solution and an aluminium plate served as two electrodes of the cell. A pulsed power supply with output voltage operating in a constant voltage mode similar to one described elsewhere,¹⁵ was used for the etching process. Under darkness, the 120 s etching process was carried out by applying a pulsed current between the two electrodes; at peak current density of 10 mA cm⁻² with pulse duration of 10 ms. After etching, the cell was rinsed with de-ionized water, dried in N₂ stream.

Current–voltage characteristics were measured at room temperature before and after etching and investigated under several low illumination levels. Measurements were performed using a Keithley 238 Source Measure Unit (SMU) through a four-point connection. Halogen lamps were used for illumination, whereas a silicon calibration cell was used to set the illumination level. The illumination level was varied between 0 (dark) and 32 mW cm⁻². In order to analyse cell photocurrent spectral response and reflectivity measurements were performed using an Optosolar spectrophotometer system SR 300 equipped with an integrating sphere in the wavelength range of 400–1100 nm.

3. Results and discussion

Figure 1 shows scanning electron microscope (SEM) photographs for the cell; (a) before and (b) after etching. The clear change in the surface topography after etching process represents an evidence of porous silicon formation.

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Table 1. Data of the cell Q6-1380 provided by Q-Cells AG, Germany. The studied cell was a 1.2 cm^2 partition of this cell.

Product	Multi-crystalline silicon solar cell
Format	$150 \text{ mm} \times 150 \text{ mm} \pm 1 \text{ mm}$
Thickness	$300 \pm 40 \mu\text{m}$
Front (–)	2 mm bus bars (silver), blue anti-reflection coating (silicon nitride)
Back (+)	5 mm wide soldering pads (silver/aluminium), back surface field (aluminium)

Figure 1. Surface SEM photographs for the cell before and after etching. Etching was performed for 2 min.

The white line represents the bus bar that forms the front contact. Although the front contact is slightly damaged due to etching, cell characteristics could be measured as it will be demonstrated below.

Figure 2 shows the j - V curves measured at room temperature for various illumination level values between $I_{\text{ill}} = 0$ (dark) and $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$ for the mc-Si cell before and after etching. From this figure the photovoltaic parameters (short-circuit current density, open-circuit voltage, fill factor and solar cell conversion efficiency) were obtained and are presented in figure 3 depending on illumination intensity.

Figure 3 clearly shows that both short-circuit current density and open-circuit voltage increase with the increase in illumination intensity, and that their values for the etched cell are higher than the corresponding values before cell etching. In particular, the short-circuit current density increases from $j_{\text{sc}} = 0.136 \text{ mA cm}^{-2}$ (at an illumination intensity of $I_{\text{ill}} = 5.55 \text{ mW cm}^{-2}$) to $j_{\text{sc}} = 10 \text{ mA cm}^{-2}$ (at an illumination intensity of $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$) before etching, while after etching it increases from $j_{\text{sc}} = 0.1$ to $j_{\text{sc}} = 12.7 \text{ mA cm}^{-2}$ at the corresponding illumination intensity values. Open-circuit voltage also increases from $V_{\text{oc}} = 0.286 \text{ V}$ (at an illumination intensity of $I_{\text{ill}} = 5.55 \text{ mW cm}^{-2}$) to $V_{\text{oc}} = 0.542 \text{ V}$ (at an illumination intensity of $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$) before etching, while after etching it increases from $V_{\text{oc}} = 0.256 \text{ V}$ to $V_{\text{oc}} = 0.547 \text{ V}$ at the corresponding illumination intensity values. While fill factor values of the cell before etching increase with the increase in illumination intensity (from $\text{ff} = 51\%$ at an illumination intensity of $I_{\text{ill}} = 5.55 \text{ mW cm}^{-2}$ to $\text{ff} = 69\%$ at an illumination intensity of $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$), those values of the etched cell increase for low illumination intensity values up to a certain value ($\text{ff} = 62\%$

Figure 2. Dependence of the j - V characteristics of the mc-Si cell before and after etching on illumination intensity. The illumination was performed using a halogen lamp, and the illumination intensity was varied between $I_{\text{ill}} = 0$ (dark) and $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$ using neutral density filters.

Figure 3. Dependence of the photovoltaic parameters (short-circuit current density, open-circuit voltage, fill factor and solar cell conversion efficiency) on illumination intensity.

at an illumination intensity of $I_{\text{ill}} = 19.33 \text{ mW cm}^{-2}$, and then start to decrease with the increase in illumination intensity, and it reaches the value of $\text{ff} = 58\%$ at an illumination intensity of $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$. Altogether the solar cell conversion efficiency values remain higher for the etched cell than for the cell before etching for all illumination intensity values (for instance at an illumination intensity of $I_{\text{ill}} = 32 \text{ mW cm}^{-2}$ the solar cell conversion efficiency value before etching is $\eta = 11.6\%$, while the corresponding efficiency value after etching is $\eta = 12.5\%$).

In order to explain this behaviour spectral response and reflectivity measurements were performed before and after etching. Figure 4a shows spectral response of both cells in the wavelength range between 400 and 1100 nm. It clearly shows that the spectral response of the etched cell is higher than that for the cell before etching in the entire wavelength range. This explains the higher short-circuit current density—and therefore also higher open-circuit voltage values—of the

etched cell than those of the cell before etching. This statement is confirmed through reflection measurements of both cells, which are presented in figure 4b. This figure demonstrates that cell etching leads to a decrease in the reflection. In the literature porous silicon is proposed to act as an antireflection layer.^{10–12}

In order to quantify the short-circuit current increase after etching the external quantum efficiency was calculated from the spectral response measurements using the equation

$$\text{SR}(\lambda) = \frac{\lambda Q_{\text{ext}}(\lambda)}{hc}, \quad (1)$$

where the quantities λ , $\text{SR}(\lambda)$, $Q_{\text{ext}}(\lambda)$, h , c are respectively, the wavelength, the spectral response, the external quantum efficiency, the Planck constant and the speed of light in a vacuum.

The short-circuit current was then calculated from the spectral quantum efficiency folded with the halogen lamp

Figure 4. (a) Spectral response and (b) reflection of the studied cell before and after etching.

spectrum and integrated over the relevant wavelength range between 400 and 1100 nm using the equation

$$j_{sc} = q \int_{400}^{1100} Q_{ext}(\lambda) \Phi(\lambda) d\lambda, \quad (2)$$

where $\Phi(\lambda)$ is the illumination spectrum.

The intensity of the illumination spectrum was set so that the integration reveals a short-circuit current of $j_{sc} = 10 \text{ mA cm}^{-2}$ for the solar cell before etching. Calculation of the short-

circuit current density for the solar cell after etching using the same procedure with the same illumination intensity (which was set for the cell before etching) revealed a short-circuit current density of $j_{sc} = 12.66 \text{ mA cm}^{-2}$, with a good agreement of the experimental value of $j_{sc} = 12.7 \text{ mA cm}^{-2}$.

The interpretation of the fill factor behaviour is more complicated than that of both short-circuit current and open-circuit voltage. For this interpretation current–voltage characteristics at each illumination intensity should be analysed.

In a recent work, a modified two-diode equivalent circuit accounting for an additional ohmic series resistance in the vicinity of grain boundaries was proposed in order to accurately describe current–voltage characteristics of mc-Si solar cells, especially under low illumination levels.¹⁶ The essential features of this model are presented below.

The model is based on the assumptions that the cell consists of two different regions with different current transport mechanisms: the crystalline region and the grain boundary region, accounted by the two parallel diodes D_1 and D_2 in the equivalent circuit, respectively. The grain boundary region exhibits an additional series resistance since the resistivity in the vicinity of grain boundaries is higher than that within the crystallites.¹⁷ This is accounted for by R_{s2} , which is connected to D_2 in figure 5. A shunt resistance R_{sh} is connected in parallel to both diodes D_1 and D_2 . Furthermore, a series resistance R_s is connected to all three branches. The equations describing current transport through the cell contain variable diode ideality factors, so that there are no restrictions of current transport mechanisms.

In accordance with this equivalent circuit, the total current that flows through the cell can be written as follows:

$$j(V) = j_1(V) + j_2(V) + \frac{(V - j(V)R_s)}{R_{sh}} + j_{ph}. \quad (3)$$

Here R_s is the series resistance, R_{sh} the shunt resistance and j_{ph} the photo-current. The quantities $j_1(V)$ and $j_2(V)$

Figure 5. Modified two-diode equivalent circuit used in this study for analysing the multi-crystalline silicon solar cell.

Table 2. Cell fitting parameters before etching.

I_{ill} (mW cm ⁻²)	I_{ph} (mA cm ⁻²)	n_1	n_2	j_{01} (A cm ⁻²)	j_{02} (A cm ⁻²)	R_s (Ω cm ²)	R_{s2} (Ω cm ²)
5.55	0.16	1.03	2.82	6.38×10^{-12}	3.14×10^{-6}	0.32	4.10×10^{-4}
7.4	0.37	1.02	3.00	6.38×10^{-12}	4.18×10^{-6}	0.37	4.10×10^{-4}
9.27	0.76	1.02	2.99	4.24×10^{-12}	4.39×10^{-6}	0.32	4.10×10^{-4}
11.12	1.35	1.02	2.99	4.24×10^{-12}	4.39×10^{-6}	0.32	4.10×10^{-4}
13.97	2.16	1.02	2.99	4.25×10^{-12}	4.63×10^{-6}	0.32	8.97×10^{-5}
14.82	3.19	1.02	2.99	4.25×10^{-12}	4.63×10^{-6}	0.32	8.97×10^{-5}
16.67	4.50	1.01	2.99	4.42×10^{-12}	4.81×10^{-6}	0.30	6.20×10^{-5}
19.33	5.85	1.01	2.99	4.42×10^{-12}	4.81×10^{-6}	0.30	6.20×10^{-5}
22.33	7.55	1.02	2.96	5.06×10^{-12}	4.93×10^{-6}	0.30	6.20×10^{-5}
25.67	9.40	1.02	2.96	5.21×10^{-12}	4.93×10^{-6}	0.32	6.20×10^{-5}
29	9.97	1.02	2.96	5.08×10^{-12}	4.93×10^{-6}	0.34	6.20×10^{-5}
32.33	12.10	1.03	2.96	7.87×10^{-12}	4.93×10^{-6}	0.34	6.20×10^{-5}

Table 3. Cell fitting parameters after etching.

I_{ill} (mW cm ⁻²)	I_{ph} (mA cm ⁻²)	n_1	n_2	j_{01} (A cm ⁻²)	j_{02} (A cm ⁻²)	R_s (Ω cm ²)	R_{s2} (Ω cm ²)
5.55	0.13	0.94	2.79	1.75×10^{-13}	3.33×10^{-6}	0.13	0.02
7.4	0.40	0.94	2.79	1.75×10^{-13}	3.33×10^{-6}	0.13	0.02
9.27	0.87	0.94	2.79	1.75×10^{-13}	3.33×10^{-6}	0.13	0.02
11.12	1.52	0.94	2.74	1.75×10^{-13}	3.00×10^{-6}	0.13	0.02
13.97	2.39	0.94	2.74	1.75×10^{-13}	3.17×10^{-6}	0.13	0.02
14.82	3.54	0.94	2.74	1.75×10^{-13}	3.62×10^{-6}	0.13	0.88
16.67	4.86	0.94	2.74	1.75×10^{-13}	3.92×10^{-6}	0.13	0.90
19.33	6.43	0.94	2.74	1.75×10^{-13}	4.38×10^{-6}	0.13	0.91
22.33	8.30	0.94	2.74	1.75×10^{-13}	4.83×10^{-6}	0.13	0.92
25.67	10.35	0.94	2.74	2.31×10^{-13}	7.00×10^{-6}	0.13	2.95
29	12.60	0.94	2.74	2.90×10^{-13}	8.76×10^{-6}	0.14	3.52
32.33	15.20	0.94	2.74	3.01×10^{-13}	1.10×10^{-5}	0.13	3.73

represent currents that flow through diode D_1 and diode D_2 , respectively, and can be written as

$$j_1(V) = j_{01} \left\{ \exp \left[\frac{q(V - j(V) R_s)}{n_1 k T} \right] - 1 \right\}, \quad (4)$$

$$j_2(V) = j_{02} \left\{ \exp \left[\frac{q(V - j(V) R_s - j_2(V) R_{s2})}{n_2 k T} \right] - 1 \right\}, \quad (5)$$

where j_{01} and j_{02} are the saturation current densities, n_1 and n_2 the diode ideality factors, q the electron charge, k the Boltzmann constant, T the absolute temperature and R_{s2} an additional series resistance connected to D_2 .

The analysis of current–voltage characteristics revealed that the shunt resistance is very high so that its effect on all characteristics can be neglected. The fitting method used was a least-squares method. The obtained diode parameters are presented in tables 2 and 3, and illustrated in figure 6 for the cell before and after etching.

The value of the diode ideality factor n_1 of the first diode D_1 is close to 1 for both diodes before and after etching, this indicates that current transport in the first diode is dominated

by recombination in the depletion layer, allocated to a recombination in the crystalline region.¹⁷ As illustrated in figure 6 the changes in n_1 due to etching can be neglected. This means that etching does not significantly affect recombination in the crystalline region. The diode ideality factor n_2 of the second diode D_2 is greater than 2, which indicates that current transport in the second diode is dominated by recombination at grain boundaries. The values of n_2 are reduced after etching indicating reduced grain boundary recombination. The saturation current density values j_{01} of D_1 are reduced by approximately two orders of magnitude after etching, whereas the corresponding values of D_2 are lower at low illumination intensity values and higher at high illumination intensity values after etching. The series resistance R_s slightly decreases after etching. The reduction of n_1 , j_{01} and R_s in D_1 after etching represents an advantage in diode behaviour, whereas the disadvantage of etching seems to appear in the increase of j_{02} and R_{s2} in D_2 . At illumination intensity values up to $I_{\text{ill}} \approx 13$ mW cm⁻² R_{s2} increases slightly after etching, with increasing illumination intensity values higher than that value R_{s2} increases by approximately two orders of magnitude. In order to explain this behaviour we assume that etching destroys the surface of mc-Si cell forming porous silicon.

Figure 6. Parameters describing the cells before and after etching.

This porous layer is high resistive and it is difficult to determine its exact value.^{18,19} This leads to a high series resistance R_{s2} . This resistance leads to considerably high losses in solar cell fill factor, as it will be demonstrated below.

In order to demonstrate the effect of R_{s2} on the cell characteristics the contribution of each of the two diodes (D_1 and D_2) to the measured characteristic is presented in figure 7 for the measured characteristics at an illumination intensity of $I_{\text{ill}} \approx 22 \text{ mW cm}^{-2}$ before and after etching. In this figure, calculated j_1 and j_2 using equations (3) and (4) and the data

presented in tables 2 and 3 are plotted vs. V together with their sum $j_1 + j_2$.

Figure 7 clearly demonstrates the immense effect of R_{s2} on the cell characteristics after etching, especially in the range of 0–0.4 V. This range is usually used to determine cell fill factor. Before etching the values of R_{s2} are not so high to considerably affect the cell characteristics and cell fill factor.

4. Conclusion

Porous silicon formation on the top of mc-Si solar cells layer has an advantage that it reduces photocurrent losses due to reduced reflection at its surface, and therefore it enhances short-circuit current density and open-circuit voltage values. However, it has a disadvantage that it is high resistive and therefore it leads to considerably high losses in solar cell fill factor. Investigation in fill factor improvement through reducing porous silicon resistivity might be an important goal.

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Figure 7. Calculated contributions of D_1 and D_2 to the measured characteristic at an illumination intensity of $I_{\text{ill}} = 22 \text{ mW cm}^{-2}$ before and after etching.