

THE INDUSTRIAL TECHNOLOGY OF CRYSTALLINE SILICON SOLAR CELLS

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The technology used to produce silicon solar cells in the Institute of Metallurgy and Materials Science (IMMS) in Cracow is presented. The process sequence is based on diffusion from POCl_3 and screen printed contacts fired through the SiN_x or TiO_x antireflection coating (ARC). Co-firing of the back and front metallization was achieved in an IR furnace. Two new methods of acid texturization are discussed. The first is based on the formation of a porous layer with of pore diameter about $0.5 \mu\text{m}$, whilst the second is in the form of craters of size $5\text{-}10 \mu\text{m}$. The Cz-Si monocrystalline solar cells have an efficiency greater than 15% with both TiO_x ARC and SiN_x ARC. The mc-Si have an efficiency over 14% with KOH texturization and with SiN_x ARC. The parameters of solar cells with different kinds of texturization, with SiN_x and with TiO_x ARC are shown and analyzed.

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1. Introduction

The substrates used in this work were 'as-cut', boron doped p-type, $1 \Omega\cdot\text{cm}$ (100), CZ-silicon and multicrystalline (mc-Si) wafers supplied by Bayer Solar Corporation. The thickness of the wafers was $300 \mu\text{m}$ and area $10 \text{ cm} \times 10 \text{ cm}$. The specified carrier minority lifetime of Cz-Si wafers was $\geq 10 \mu\text{s}$ and minority carriers diffusion length of mc-Si wafers was $\sim 80 \mu\text{m}$. The manufacturing sequence for the cell fabrication can be divided in the following main stages:

- 1). Chemical etching
- 2). Emitter formation
- 3). Parasitic junction removal
- 4). Passivation
- 5). Antireflection coating
- 6). Screen-printing contacts
- 7). Co-firing front and back contacts

When using SiN_x as the ARC the seven technological steps shown above can be reduced to six. This is because the SiN_x layer provides a very effective passivation layer which can replace the thermally applied SiO_2 layer. Additionally it is known that deposition of the $\text{SiN}_x\text{:H}$ layer by PECVD method is a most important process for high efficiency mc-Si. This is caused by H atoms which passivate the defects in the mc-Si material and the synergistic effect of mc-Si gettering with Al back layer is also observed [1,2].

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2. Experimental

2.1 Chemical etching

The wafers were etched in 30 % KOH solution in order to remove the surface layers about 10 μm thick damaged by sawing followed by the texturization in the KOH:IPA:H₂O solution. After this process, the monocrystalline Si wafers with (100) surface orientation were covered by microscopic pyramids with (111) crystallographic planes. In the case of multicrystalline wafers this method is not very effective because the crystalline grains have different crystallographic orientation (Fig. 1a) and the effective reflectance in the range 400 – 1100 nm is only 24 %. A very promising method of texturization of mc-Si is by acid chemical etching in HF:HNO₃:H₂O solution [3]. This method is being developed at IMMS. Fig. 1b shows the micrograph of the mc-Si after acid texturization for 1 minute.

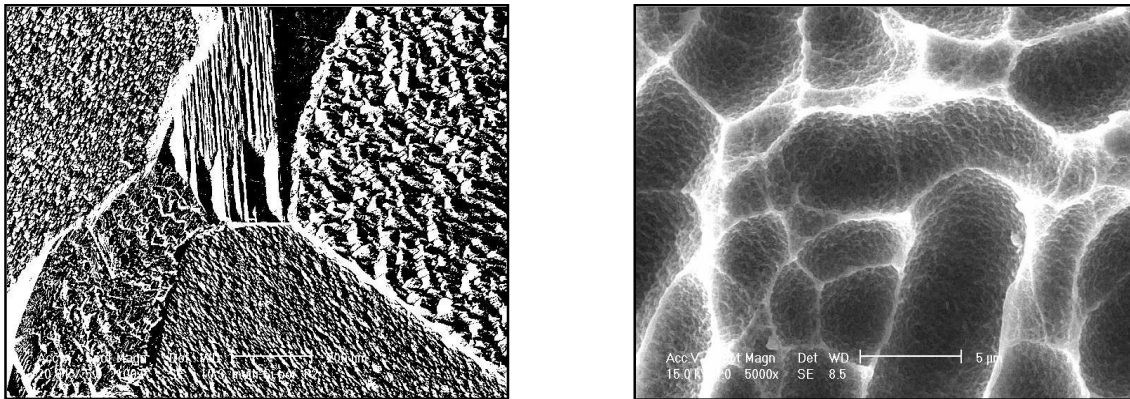


Fig. 1. Multicrystalline silicon surface after removal saw damage and texturization in KOH solution (a) and after acid texturization in HF:HNO₃:H₂O solution (b).

The etching rate of silicon is about 5 $\mu\text{m}/\text{min}/\text{face}$. The removal of saw damage and the surface texturing is obtained in a single step. Fig. 1b shows the structure of the texturized surface. The surface is covered by craters whose size is about 5-10 μm and small pits inside the craters can be observed.

Another method which is under development is the application of porous silicon onto mc-Si solar cells. Most research effort were put into porous silicon (PS) formation after donor doping which effects the antireflection coating and the selective emitter [4,5] but PS produced before phosphorous diffusion is still rarely published.

The complications in applying PS onto mc-Si solar cells is well known, but it has the potential to increase the efficiency, especially for improving the short-circuit current through the following effects:

- o Reduction of front surface reflection
- o Absorption of base of photons closer to the collecting junction
- o Trapping of weakly absorbed photons within the thin cell (light trapping)

The porous layer was prepared in a HF-HNO₃ based solution (C1 solution) on a p-type 1 $\Omega\cdot\text{cm}$ mc-Si after saw damage layer removal in KOH solution. Next the PS layer was modified in 98HNO₃-2HF solution (C2 solution) for a time in the range 0 to 300 seconds as own in Fig. 2. An effect of etching in C2 solution is the formation of the porous structure. The pores produced are of approximately 0.5 μm diameter so the structure can be classified as a macroporous structure. This structure is, in contrast to a nanoporous structure, resistant to high temperature treatment during the diffusion process. The modification of the surface by etching in C2 solution changes the diameter of

the pores and has a strong influence on the light reflectivity of the surface and the sheet resistance of the emitter after the diffusion process. This modification is crucial for the final parameters of the solar cells which are given below.

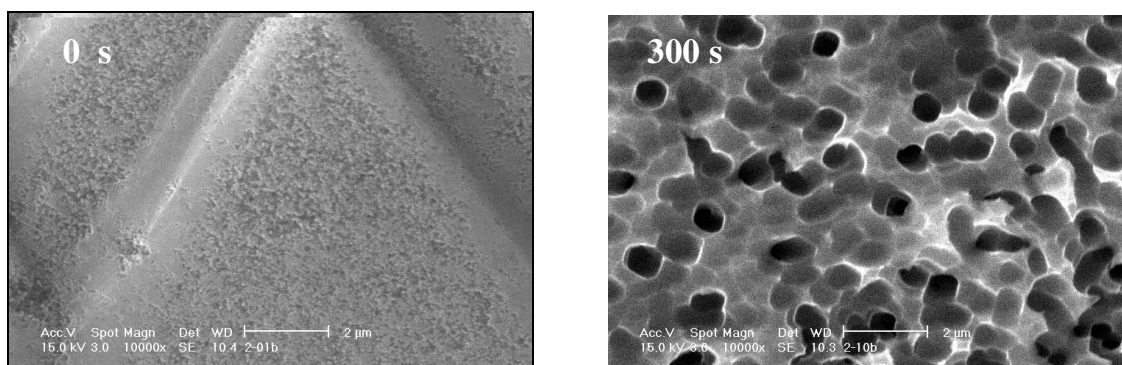


Fig. 2. SEM micrographs of porous silicon layers without modification and after modification in $98\text{HNO}_3\text{-2HF}$ solution for 300 seconds. (The removal of saw damage was in KOH solution).

Reflection measurements from PS layers shown in Fig. 3 were carried out using a Perkin-Elmer Lambda-9 spectrophotometer equipped with an integral sphere.

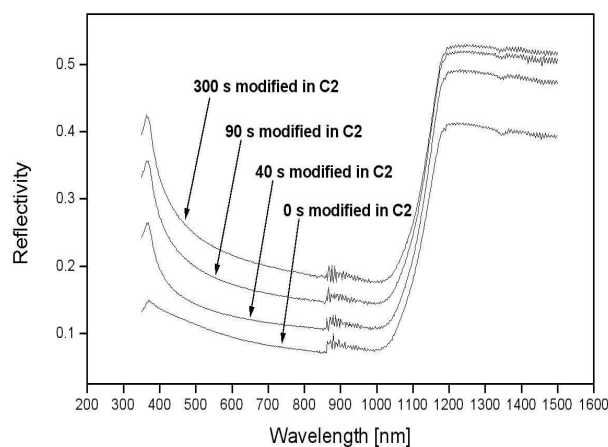


Fig. 3. Reflectivity of porous silicon layers after modification in $98\text{HNO}_3\text{-2HF}$ (vol.) solution (C2) for 0 – 300 seconds.

2.2 Emitter formation

The emitter formation is one of the crucial steps in the manufacturing process of silicon solar cells. The emitter “n⁺” was generated in an open quartz tube using liquid POCl_3 as the doping source at temperatures in the range $845\text{--}890\text{ }^\circ\text{C}$ for 40 minutes. This produces an emitter with a sheet resistance in the range from $20\ \Omega/\square$ to $40\ \Omega/\square$ as measured with a four point probe. The diffusion profiles determined by secondary ion mass spectroscopy (SIMS) measurements are presented in Fig. 5.

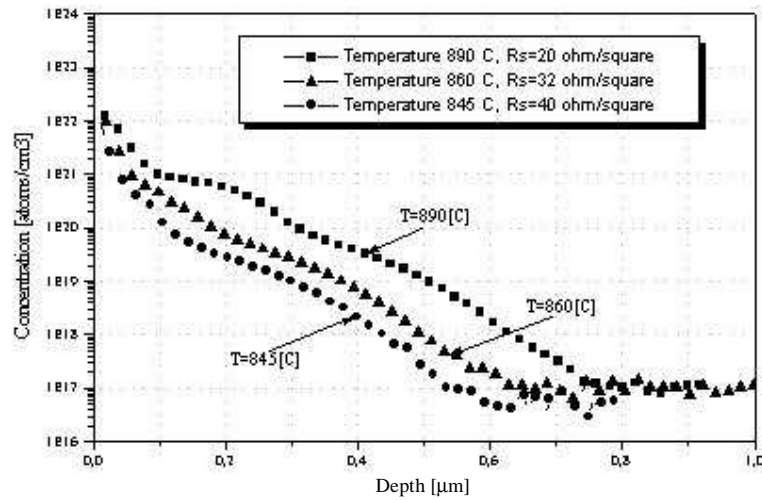


Fig. 5. Phosphorous concentration profiles at a diffusion time of 40 minutes in relation to the diffusion temperature after processing using POCl_3 , determined by SIMS.

2.3 Parasitic junction removal and chemical etching

After diffusion the wafers are covered by phosphorus-silicate glass PSG and have a donor doping layer on both sides and edges. At first the parasitic junction was removed in $\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH}$ solution. Then the PSG was removed in a 10 % HF solution for 2 minutes and the wafers were dried in a spin-drier in an atmosphere of highly purified air.

2.4 Passivation process

In order to obtain high efficiency it is necessary to reduce the surface recombination losses. The standard technique for the reduction of the surface state density of Si is thermal oxidation. In the experiment the thin SiO_2 layer was created at 800 °C for 15 min in dry oxygen. As stated above this process is not necessary in the case if $\text{SiN}_x:\text{H}$ is applied as antireflection coating.

2.5 Antireflection coatings

Two kinds of ARC coatings were deposited, either TiO_x or $\text{SiN}_x:\text{H}$. The TiO_x antireflection coating was deposited by sprayed-on using tetraethylorthotitanat ($(\text{C}_2\text{H}_5\text{O})_4\text{Ti}$) compounds. Depositing at 300 °C for 5 seconds resulted in a 80 nm thick layer. The main advantages of this method are simplicity and a very big throughput. The method is very suitable for solar cells based on Cz-Si wafers but for multicrystalline cells the $\text{SiN}_x:\text{H}$ deposition by PECVD is more profitable.

Fig. 6 shows the reflectance of the Si texturized, passivated surface with and without the layer of TiO_x ARC and of mc-Si with a SiN_x layer.

2.6 Screen – printing and co-firing of metal contacts

The screen-printing process is very simple and commonly used in industrial production [6,7]. A few types of photovoltaic pastes were tested and eventually silver paste, PV145, manufactured by Du Pont, was used on the front and was printed using 330 mesh screens. The lines width of the finger

was 150 μm and the spacing between the metal fingers 2.5 mm. The coverage of the top surface cell by grid contact was 7%.

The back contact covering the full rear surface was deposited with pure Al paste. The two collection back bus bar contacts were printed with a silver paste containing 3% (w.g.) aluminium paste. After screen printing, the pastes were dried by heating at 200°C and subsequently fired at about 700 °C in an infrared furnace (IR) for about 13 seconds.

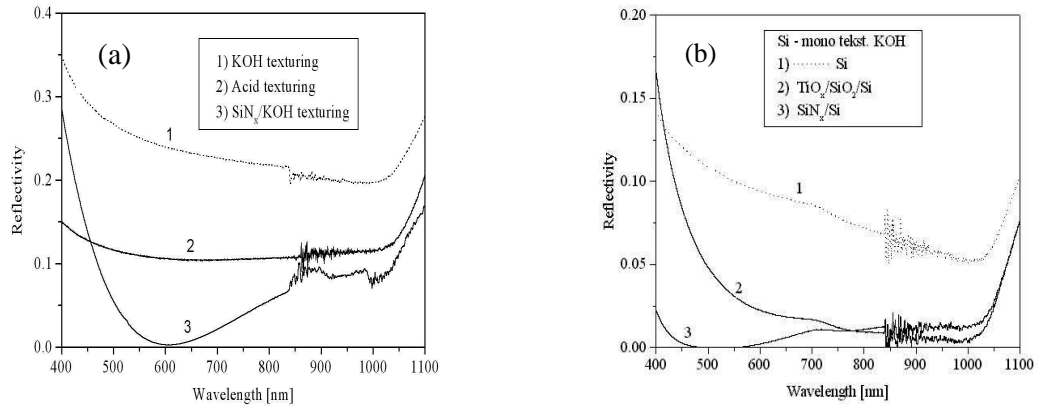


Fig. 6. Reflectivity from mc-Si (a) and from Cz-Si (b) with and without ARC.

3. Results

The parameters of the solar cells were measured under standard simulated AM 1.5 (100 mW/cm^2) radiation at 24°C. The results are presented in Table 1.

The measurements of I-V characteristics allow the basic parameters like: I_{sc} - short circuit current, V_{oc} - open circuit voltage, FF – fill factor and E_{ff} – efficiency to be determined. The I-V curves were fitted with the double exponential relationship of the following form:

$$I = I_{\text{ph}} - I_{s1} \left[\exp\left(\frac{V + I \cdot R_s}{A_1 V_t}\right) - 1 \right] - I_{s2} \left[\exp\left(\frac{V + I \cdot R_s}{A_2 V_t}\right) - 1 \right] - \frac{V + I \cdot R_s}{R_{\text{sh}}} \quad (1)$$

where: I_{ph} - generated photocurrent, R_s - series resistance, R_{sh} - shunt resistance, A_1 and A_2 diode ideality factors, I_{s1} and I_{s2} saturation currents. V_t is equal to kT/e where k , e and T have their usual meaning. In order to accomplish this task, an interactive computer program was used [8]. A_1 equals 1.0 and A_2 equals 2.0 was applied. In such a case, the first diode represents the diffusion current, which is connected with the neutral regions, either emitter or base, whereas the second diode is attributed to generation-recombination phenomena in the space charge region of solar cell.

3.1 Solar cells with alkaline texturization

The typical parameters of solar cells 10×10 cm monocrystalline and multicrystalline with TiO_x and with SiN_x ARC are given in Table 1 where $r_s = R_s \times \text{area}$, $r_{\text{sh}} = R_{\text{sh}} \times \text{area}$, J_{s1} , J_{s2} , – density of the saturation currents, J_{sc} – density of the short circuit current.

Table 1. Typical electrical parameters of 100 cm² solar cells.

No.	Si	ARC	r_s Ωcm^2	r_{sh} $\text{k}\Omega\text{cm}^2$	J_{s1} pA/cm^2	J_{s2} nA/cm^2	J_{sc} A	V_{oc} mV	FF %	E_{ff} [%]
1	Cz-Si	TiO _x	0.8	4.5	1.8	37.4	32.8	604	76.5	15.1
2	Cz-Si	SiN _x	0.8	1.1	1.6	51.0	33.4	603	76.0	15.3
3	mc-Si	TiO _x	0.1	1.1	3.3	98.1	29.2	580	76.8	13.0
4	mc-Si	SiN _x	0.7	2.2	1.7	90.1	31.7	596	75.2	14.2

3.2 Solar cells with acid texturization

The parameters of experimental solar cells 5 × 5 cm with acid texturization and with TiO_x antireflection coatings are given in Table 2. For comparison the parameters of solar reference with KOH texturization are also shown in the table.

Table 2. The parameters of 5 × 5 cm² mc-Si solar cells with acid texturization.

No.	r_s Ωcm^2	r_{sh} $\text{k}\Omega\text{cm}^2$	J_{s1} pA/cm^2	J_{s2} nA/cm^2	J_{sc} mA/cm^2	V_{oc} mV	FF %	E_{ff} %
1	0.64	1.0	2.1	119	31.2	590	73.8	13.6
2	0.58	2.7	1.8	91.0	30.1	595	75.5	13.5
refer.	0.82	5.7	2.4	72.5	29.9	591	75.7	13.4

3.3 Solar cell with macroporous silicon layers.

The experimental parameters of 5 × 5 cm mc-Si with a porous layer obtained by chemical acid etching and after subsequently modification in 98HNO₃-2HF (C2 solution) are given in Table 3.

Table 3. The parameters of 5 cm × 5 cm mc-Si solar cells with porous silicon layer for different times of modification in 98 HNO₃-2 HF solution.

No.	time s	R_s Ω/\square	r_s Ωcm^2	r_{sh} $\text{k}\Omega\text{cm}^2$	J_{s1} pA/cm^2	J_{s2} nA/cm^2	J_{sc} mA/cm^2	V_{oc} mV	FF %	E_{ff} %
1	0	55	0.5	0.4	4.1	465	29.1	549	68.1	10.9
2	40	36	0.5	0.4	4.2	92.6	29.0	574	73.9	12.3
3	90	35	0.5	1.0	4.6	81.9	29.0	574	75.8	12.6
4	300	37	0.5	2.2	2.5	96.5	30.2	587	75.9	13.5
refer.	-	44	0.6	2.5	3.5	141.0	29.8	577	74.8	12.9

For comparison the parameters solar cell without any porous layer is placed (named as refer.). The influence of etching in C2 solution (before diffusion) on sheet resistance of the emitter is shown. It can be seen that the etching in C2 solution is necessary to obtain satisfactory values for FF and V_{oc} .

4. Discussion

The best solar cells have been obtained with Cz-Si with a SiN_x layer. The typical efficiency was about 15.5 %. Solar cells with a TiO_x layer and thermal passivation are about 15 % efficient. The typical solar cells with SiN_x have an efficiency of about 14.2 % and with TiO_x the efficiency is

significantly less - about 13 %. It is clear that in the case of multicrystalline silicon the major difference between the efficiencies is mainly caused by defect passivation by atomic hydrogen from the $\text{SiN}_x\text{:H}$ layer during firing of the metallization. A large increase of the V_{oc} and I_{sc} observed which is caused by the decreasing of the diodes saturation currents, mainly J_{s1} , which can be explained by an increase of the minority carriers diffusion length.

The solar cells with acid texturization have J_{sc} about 4.3 % greater than for the reference solar cell with KOH texturization. In the case of a solar cell with a porous layer only 1.3 % increase of J_{sc} is noticed. The efficiency of these solar cells is about 13.5 % and is higher than for solar cells with KOH texturization.

5. Conclusions

The very simple method of TiO_x deposition allows an efficiency of 15 % for monocrystalline silicon and about 13% for multicrystalline silicon of 10×10 cm to be obtained. In the case mc-Si considerable improvement is obtained if $\text{SiN}_x\text{:H}$ is applied by PECVD. The differences between monocrystalline and multicrystalline silicon solar cells with SiN_x ARC are decreasing. This difference will be smaller if more effective texturization can be applied.

The 5×5 cm experimental solar cells with porous silicon and with acid texturization are very promising. 30.2 mA/cm^2 has been obtained for solar cells with a porous layer and 31.2 mA/cm^2 for solar cell with acid texturization. The V_{oc} for cell acid texturized was 595 mV which is comparable to solar cells KOH texturization with a SiN_x layer.

It is expected that application of $\text{SiN}_x\text{:H}$ for solar cells with a porous layer or with acid texturization will increase the efficiency of mc-Si solar cells to 15-16 %.

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References

- [1] A. Rohatgi, V. Yelundur, J. Jeong, A. Ebong, D. Meier, A. M. Gabor, M. D. Rosenblum, Proc. of the 16th European Photovoltaic Solar Energy Conf., Glasgow, UK, (2000)1120.
- [2] F. Duerinckx, J. Szlufcik, Solar Energy & Solar Cells **72**, 231(2002).
- [3] R. E. Einhaus, E. Vazsonyi, F. Duerickx, J. Horzel, E. Van Kerschaver, J. Szlufcik, J. Nijs, R. Mertens, Proc. of the Second World Conf. on Photovoltaic Energy Photovoltaic Energy Conversion, Vienna, Austria, 1630, 1998.
- [4] R. R. Bilyalov, R. Lüdemann, W. Wettling, L. Stalmans, J. Poortmans, J. Nijs, L. Schirone, G. Sotgiu, S. Strehlke, C. Lévy-Clément, Solar Energy Materials & Solar Cells **60**, 391(2000).
- [5] M. Lipiński, S. Bastide, P. Panek, C. Lévy-Clément, physica status solidi (A) **197**, 512(2003).
- [6] J. Szlufcik, F. Duerinckx, E. Van Kerschaver, J. Nijs, Proc. of the 17th European Photovoltaic Solar Energy Conf., Munich, Germany, 1271, 2001.
- [7] J. Szlufcik, F. Duerinckx, J. Horzel, E. Van Kerschaver, H. Dekkers, S. De Wolf, P. Choulat, C. Allebe, J. Nijs, Solar Energy Materials & Solar Cells **74**, 155(2002).
- [8] T. Żdanowicz, Proc. of 12th European Photovoltaic Solar Energy Conf., Amsterdam, Netherlands, 1311, 1994.