# ACIDIC TEXTURISATION OF MC-SI USING A HIGH THROUGHPUT IN-LINE PROTOTYPE SYSTEM WITH NO ORGANIC CHEMISTRY

A. Hauser, I. Melnyk, E. Wefringhaus, F. Delahaye\*, G. Vilsmeier\*, P. Fath \*RENA Sondermaschinen GmbH, Ob der Eck 5, 78148 Gütenbach, Germany University of Konstanz, Department of Physics, PO Box X916, 78457 Konstanz, Germany Tel: +49-7531-88-3386, Fax: +49-7531-88-3895. Email: alexander.hauser@uni-konstanz.de

ABSTRACT: Texturing of mc-Si is becoming more and more important to increase the efficiency of industrial type solar cells. Compared to mono crystalline silicon the well established alkaline texturisation does not work well on mc-Si due to the different grain orientations. One of the most promising techniques is isotropic etching with HF, HNO<sub>3</sub> and organic additives. We have found an etch consisting of only HF and HNO<sub>3</sub> that leads to comparable improvements in reflection and I-V characteristics, but is easier to handle and less critical during the etch process. On batches of 50 wafers, using a standard PECVD-SiN screen printing process, an increase in efficiency from 14.6 % to 15.6 %, which is 7 % relative on cell level has been shown. For 36 cell modules the improvement was still 4.8 % relative compared to alkaline etched cells. Together with the company RENA an in-line etching lab system has been developed for isotropic texturing of mc-Si wafers. It has a throughput of approximately 200 wafers per line and depending on the wafer size up to 3 lines are available for this system. The overall number of etched wafers in this system since installation is 30.000. During 3 long-term tests stability of reflection and etch rate were investigated. In addition exact measurements of actual concentrations of ingredients were possible due to an online analyzer that took samples every 12 minutes.

Keywords: Multi-Crystalline - 1, Texturisation - 2, Light Trapping - 3

# 1 INTRODUCTION

The share of mc-Si used by the PV industry is continuously increasing due to the lower material costs. There are two main disadvantages compared to CZ-Si: the effective bulk lifetime of the minority charge carriers is lower and the well known and widely used alkaline texture technique leading to random pyramids is largely ineffective due to the different grain orientations in mc-Si. Several texturing techniques are under investigation, but none have reached the status of mass production for standard screen printed solar cells. The mechanical texturing with a dicing saw for example is only used for the POWER (polycrystalline wafer engineering result) solar cell concept. Reactive ion etching is used at Kyocera Corp. in an extended pilot production and only the acid texturing developed by IMEC [1], [2] has been used on large batches of wafers. This method using HF, HNO<sub>3</sub> and some additives has shown its benefit for the solar cell efficiency, but on the other hand has several aspects which are difficult to control in mass production. Some of these problems do not occur or are easier to handle with our newly developed etching solution.

# 2 ETCH SOLUTION

Compared to other acid etching solutions for Si which contain 3 or more components in addition to water, our solution consists of only 2 acids: HF and HNO<sub>3</sub>. This leads to the following advantages:

- very easy to mix;
- lower cost of etch solution;
- no organic chemicals, easier to dispose;
- very little generated heat during preparation of etch solution.

In addition the etching is carried out at temperatures below room temperature, which has the following benefits:

- little gas emission during etching and when the wafers are withdrawn;
- little generated heat during etch process;
- high stability of etch composition;
- etch speed is easier to control;
- less generation of toxic gases per unit time. The following advantages can not be assigned to a certain point, but are no less important:
- self limiting process after saw damage is removed almost no further etching;
- wafers may be etched horizontally in-line system compatible;
- suitable for cast mc-Si; for EFG, SR, Tri-Si, RGS after adaptation;
- small etching depth of app. 4.8 µm is sufficient important for thin wafers and reduced etch time.

## 3 REFLECTION

The resulting texture after the etching process has a dimension in the range of 5-10  $\mu$ m and a depth of app. 4-5  $\mu$ m.



**Fig 1:** SEM picture of an isotropic textured surface with a screen printed finger.

Compared to an alkaline etching in NaOH or KOH much lower reflectivities are obtained with the acidic texturing process. Directly after etching a reduction in average reflection from app. 36 % to app. 25 % is possible and after SiN deposition there is still a decrease from app. 10 % to 7 % (see Fig. 2).



**Fig 2:** Reflectance curves of wafers after etching and after SiN deposition. Large reductions due to texturing are obvious.

# 4 SOLAR CELL & MODULE RESULTS

After a long-term optimisation on cell level the gain through the texturing compared to alkaline etched wafers should be shown under encapsulation. Therefore a batch of 100 neighbouring mc Si wafers 12.5x12.5 cm<sup>2</sup> was split into 2 exactly comparable groups. We took the bottom of a brick; therefore the results vary from wafer 1 to wafer 50 in each group, which can be seen by efficiency in Fig. 3. After the etching our standard solar cell process was performed on the two batches which means: POCl<sub>3</sub> diffusion (55 O/sq), edge isolation by plasma etching, PSG removal, PECVD-SiN deposition, screen print of front and back contacts and fire in an IR-furnace.



**Fig 3:** Efficiencies of the cells used in the module shown below. The gain due to texturing is 1 % absolute or 7 % relative.

Afterwards the best 36 cells of each group were taken and further characterized before making modules out of them. From these 2 groups the 36 best cells of each were taken to make modules and determine the gain of the texturing under encapsulation. The best textured cell reached 16 % efficiency. The increase in efficiency of 1 % absolute means a gain of almost 7 % relative. This result has been confirmed by measuring 2 neighbouring, mean cells of each group at Fraunhofer ISE CalLab [3].

BP Solar USA made 2 modules with these cells. In Fig. 4 the more homogeneous and dark appearance of the textured module compared to the standard module can be seen.



**Fig 4:** 2 Modules made of neighbouring wafers. Left: isotextured; right: NaOH etched.

The I-V measurements of these modules show that there is still a remarkable gain in both  $I_{sc}$  (4.2 %) and power (4.8 %) relative (see Tab. 4). Despite of the fact that the original material was of varying quality (see Fig. 6, 7), an output Power of 86.5 W has been reached for the textured module. This corresponds to a cell efficiency of 15.4 %, very close to the value of the unencapsulated cells (15.6 %).

 Table I: I-V characteristics of the 2 modules shown above and calculated cell parameters.

MODULE	FF	I <sub>SC</sub>	V <sub>OC</sub>	Р
	%	Α	V	W
NaOH-etch	74.5	4.98	22.2	82.5
Isotextured	75.0	5.19	22.4	86.5
CELL	FF	J <sub>SC</sub>	Voc	Eta
	%	mA/cm <sup>2</sup>	mV	%
NaOH-etch	74.5	31.9	616.7	14.7
Isotextured	75.0	33.2	622.2	15.4
GAIN [%]	0.6	4.2	0.9	4.8

In addition to standard screen printed cells this texturing technique has been applied to buried contact cells as well. In [3] a gain in efficiency of more than 1 % absolute has been presented. Recent results will be given in [4].

#### 5 IN-LINE LAB SYSTEM

Together with the company RENA an in-line etching system has been developed for isotropic texturing of mc-Si wafers. It has a throughput of approximately 200 5" wafers per line and 3 lines are available for this system. Using only one lane also wafers larger than 210x210 mm<sup>2</sup> can be processed. The left wafer that can be seen in Fig. 5 is of this size.

Saw damage removal and texturing is done in one step. Then the wafers are rinsed and the porous silicon is removed. After having rinsed the wafers again they are dried and in principle ready for diffusion. For better cleaning of the wafers a HCl bath and also a short HF dip would be very easy to implement. Despite of this relatively high throughput of app. 600 wafers per hour this system has a footprint of less than 8 m<sup>2</sup>. Up scaling to 1700 W/h (150x150 mm<sup>2</sup>) is easy to implement and still needs less than 15 m<sup>2</sup> footprint.



**Fig 5:** Lab version of the in-line texturing equipment from RENA installed at UKN. On the left lane very large wafers can be processed (left wafer on picture is 200 mm in size).

## 6 LONG-TERM EXPERIMENTS

After having set up the in-line lab system at University of Konstanz the very good results obtained in beakers had to be transferred to this new system. Because of the different etch conditions concerning wafer position, flow of chemicals, temperature distributed and so on, the etch parameter had to be adjusted.

At the same time efforts were made to shorten the etch time to increase the potential throughput of an industrial equipment. At the end we reached an etching time of less than 2 minutes, enabling a throughput of app. 1800 wafers per hour  $(156 \times 156 \text{ mm}^2)$ .

With these new etch parameters 3 long-term tests were carried out. During these tests 7000, 10000 and 4000 wafers (>150 mm) were etched respectively. The etching was carried out continuously to simulate production conditions as close as possible. Therefore a 3 shift etch team worked at UKN. The longest test lasted for app. 65 hours without a break.

In the first long-term trial the stability of the etch conditions in terms of the resulting reflectivity of the wafers was checked. In Fig. 6 it can be seen that the mean reflection of the etched wafers only increases slightly. The fluctuations in the curve result from the dosage of chemicals that had to be done manually and therefore the etch compositions changed in discrete steps instead of continuously like in an industrial equipment.



**Fig 6:** Reflectivity of wafers taken from the first long-term test. Fluctuations result from the manual dosage of chemicals.

In the second tong-term trial the lifetime of the bath was checked. For this purpose 10.000 wafers  $156 \times 156 \text{ mm}^2$  were etched without a break. Dosing was again done manually. In this trial temperature was kept as a constant and etch velocity was regulated with the amount of dosage of HF and HNO<sub>3</sub> respectively. Doing this it was possible to keep the etch speed constant at app.  $3 \,\mu\text{m/min}$  for more than 60 hours. Afterwards no additional dosage was given and the solution was used until the etch rate dropped to app.  $2 \,\mu\text{m}$  per minute. For this test the costs of chemicals per wafer were €0.045, this is €0.012 per watt.

In the third long-term trial we tried to keep the composition of the etch solution as constant as possible. Therefore the actual concentrations of HF and HNO<sub>3</sub> were evaluated and dosage was given in an adequate manner. For this test 4000 wafers,  $156 \times 156 \text{ mm}^2$ , were used and the experiment lasted for 26 hours without a break. It can be seen in Fig. 7 that it was possible to keep the etch speed higher than 3 µm per minute by increasing the temperature throughout the experiment. The concentrations of HF and HNO<sub>3</sub> could not be kept exactly at the origin concentrations, because for dosage diluted chemicals are used and therefore it is more difficult to counterbalance a reduction of one chemical without replacing a large amount of the composition.



**Fig 7:**  $2^{nd}$  long-term test. 4000 wafers (156x156 mm<sup>2</sup>) were etched during 26 h. Temperature, etch rate and composition of etch solution were recorded regularly.

## 7 PROCESSING IN INDUSTRY

Most of the 30.000 wafers textured in this lab system were finally processed in industry at very different sites. After having gone through a learning curve concerning handling, SiN deposition and firing, which are the most critical points that have to be adjusted for these textured wafers, almost all manufacturers came to very promising results. In Fig. 8 the gain in current compared to a neighbouring reference group is shown. In this case the increase is app. 6 % relative which is quite good. Even if there is a small loss in  $V_{oc}$ , which is typical, or in FF, which can occur if processing is not well optimized, the gain in efficiency goes up to 4-5 % relative.



**Fig 8:**  $I_{sc}$  values of neighbouring wafers (150x150 mm<sup>2</sup>) textured at UKN and processed in industry. Gain due to texture is 6 %.

When doing cost calculation and assuming consumption costs for chemicals of 1.2 €cent per watt it becomes clear, that the amortization time for new equipment is very short.

## 8 SUMMARY

Starting with beaker experiments we have been successful in creating an etch solution consisting of only HF, HNO<sub>3</sub> and DI water with matching etch parameters that lead to a textured surface with reflections comparable to the results of other groups. Making solar cells a gain in efficiency of 7 % on batches of 50 mc-Si wafers  $(125x125 \text{ mm}^2)$  relative has been obtained. After making modules there was still a remarkable gain in output power of 4.8 %. Besides this the nice and homogeneous appearance of modules with isotropic textured wafers is an advantage of this method. After this together with the company RENA an in-line texturing equipment has been developed and the process was transferred to this machine.

Since then more than 30.000 wafers have been textured at UKN and the efficiency gain of 4-5 % relative has been shown in house and in industry as well. During three long-term experiments stability of etch conditions, reflection of wafers, and need of dosage had been tested. With an online analyzer the current concentrations of HF and HNO<sub>3</sub> could be measured. With this experience a detailed cost calculation and instruction for dosage can be given. Meanwhile this process has been commercialized and two industrial texturing systems have been sold.

## 9 REFERENCES

- [1] S. De Wolf, P. Choulat, E. Vazsonyi, R. Einhaus, E. van Kerschaver, K. De Clercq, J. Szlufcik: "Towards Industrial Application of Isotropic Texturing for Multicrystalline Silicon Solar Cells", *Proceedings. of the 16<sup>th</sup> EU-PVSEC*, Glasgow, 2000, pp. 1521-1524.
- [2] R. Einhaus, E. Vazsony, J. Szlufcik, J. Nijs, R. Mertens: "Isotropic Texturing of Multicrystalline Silicon Wafers with Acid Texturing Solutions", *Proceedings of the 26<sup>th</sup> IEEE PVSC*, Anaheim, 1997, pp. 167-170.
- [3] A. Hauser, I. Melnyk P. Fath, S. Narayanan, S. Roberts, T. M. Bruton: "A simplified process for isotropic texturing of ms-Si", *Proceedings of the WCPEC 3*, 2003, Osaka, Japan
- [4] M. McMann, I. Melnyk, E. Wefringhaus, A. Hauser, P. Fath, S. Roberts, T. Bruton, D. Jordan: "High Efficiency Buried Contact Solar Cells on Multicrystalline Silicon: an Industrial Reality" *this conference*