# WET CHEMICAL PROCESSING FOR C-SI SOLAR CELLS – STATUS AND PERSPECTIVES

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ABSTRACT: Wet chemical processes are widely used within crystalline silicon solar cell production, mainly for surface texturing and cleaning purposes. Whereas research has been focusing mainly on process development in the past, only little progress could be observed in terms of process control techniques. Within the paper current state-of-the-art wet chemical production processes are discussed and process control and quality assurance procedures (chemical, optical and electrical characterization of the wafers) are proposed. Purpose of the advanced characterization techniques is an enhancement of the process quality as well as an increase in high quality production yield. Further on, future industrial high efficiency cell processing necessitates cost effective, high quality cleaning processes especially prior to any surface passivation step. Starting from the well known semiconductor cleaning sequences, the paper motivates process simplifications and adaptations suitable for PV mass production.
Keywords: wet chemistry, process control, characterization.

## 1 INTRODUCTION

Quality assurance and process control for wet-chemical applications are becoming increasingly important in the industrial production chain to manufacture silicon solar cells. To overcome process operations based on operator experience as well as to extend overall operating times of common etching bathes, new developments for online characterisation and control will be mandatory.

Such quality control has the potential for significant cost reductions due to optimised durations between replacements of bath mixtures or shortening of processing times. In this context, the application of on-line analytical methods, either by means of chemical, optical or electrical measurement techniques, is of particular interest.

For the process development, new requirements emerge from transferring high efficiency cell processes from lab scale towards industrial production equipment. Especially higher standards for the wafer and surface cleaning at various stages within the cell process are required; nonetheless, production costs and therefore process complexity have to be kept as low as possible.

## 2 STATE OF THE ART PROCESS TECHNIQUES

Wet chemical etching processes represent standard procedures in nowadays batch or inline based production lines for crystalline silicon solar cells. In Figure 1, a typical front-end production sequence until $SiN_x$ antireflection (AR) deposition is shown. Most commonly used for surface texturisation are alkaline ($KOH/IPA/H_2O$ on Cz-Si) or acidic ($HF/HNO_3/H_2O$ on mc-Si) etching mixtures as well as for the removal of the phosphorus silicate glass (PSG) lowly concentrated HF [1]. In case of production sequences without final laser processing to separate p and n regions at the wafer edges (so called “edge isolation”), the diffused wafers are directly brought into a single side etching step, where the residual emitter is removed from the rear side of the wafer [2].

Within the attempt to further optimize the efficiency potential of standard Al-BSF based screen-printed silicon solar cells, several cleaning steps have been introduced. Nevertheless, for these cleaning steps a standard etching solution has not been developed so far, the picture remains quite unclear. Pre-cleaning of especially monocrystalline Cz-silicon wafers is gaining importance due to the removal of remaining organic residuals and therefore an increased homogeneity of the subsequent alkaline texturing step. Mostly alkaline cleaning solutions similar to common SC1 (standard clean 1 – $NH_4OH$ / $H_2O_2$) known from semiconductor processing are used [3, 4]

| Process | Purpose | Chemicals |
|---|---|---|
| Pre-Clean | Removal of organics | e.g. SC1, $O_3$ |
| Texturing | Surface structuring | $HF / HNO_3 / H_2O$<br>$KOH / IPA / H_2O$ |
| Cleaning | Metal removal, surface | e.g. HCl, HF, $O_3$, $H_2O_2$ |
| (Diffusion) | | |
| Rear etch (single side) | Edge isolation | $HF / HNO_3 / H_2O$ |
| PSG removal | Oxide removal | HF, ($NH_4F$) |
| Cleaning | Native oxide removal | e.g. PV160, SC1, HF / $O_3$,… |
| (AR deposition) | | |

**Figure 1:** Front-end processing of standard mc- or Cz-silicon solar cells. Various wet chemical etching and cleaning steps are applied, for cleaning purposes a large variety of different chemicals are applied.

Prior to diffusion, remaining alkali metal contaminants from the texturing process are removed by a second, additional cleaning step. Further on, especially for subsequent inline diffusion processes where the diluted phosphorus acid is deposited on the wafer as dopant source, the cleaning step also acts as “conditioner” to create a hydrophilic wafer surface. This ensures sufficient wetting of the wafer with the phosphorus acid

[5]. Therefore, HCl and HF "dips" are used for the cleaning after texturing, hydrophilisation of the surface is typically reached by applying ozone, either gaseous or with ozonised DI water [6].

For additional surface preparation prior to $SiN_x$ deposition, ECN developed a specialized selective etching mixture (commercial product name is "PV160" from Mallinckrodt Baker), which removes the highly P-concentrated top surface emitter layer (so called "dead layer") especially observed after inline diffusion processes [7]. This removal results in a better blue response and therefore typically in slightly higher $V_{oc}$ and $j_{sc}$ values of the final solar cells. Similar performance can show again the already mentioned SC1 mixture or HF / ozone treatments.

For wet chemical processes only a few applications for process monitoring already exist, mainly for the texturing processes. Where constant analysis is performed, inline titration systems are the common solution and commercial systems designed for PV applications are available. However, the systems are limited in their analysis accuracy (especially for more complex etching mixtures) as well as expensive in maintenance [8]. Alternative analysis techniques like (N)IR-spectroscopy, UV/Vis, ion chromatography or simple surface tension determination are currently under investigation in several research groups .

## 3 PROCESS CONTROL STRATEGIES

Continuous quality control will lead to significant cost reduction potentials due to

- an increase in process quality and stability resulting in an increased overall production yield,
- optimized durations between replacements of bath mixtures or shortening of processing times.

Additionally, from a scientific point of view, a better understanding of the underlying mechanisms especially for the texturing processes could be achieved, which in the end again will support further process optimization. As an example for the importance of an elaborate process control, chemical consumption data for a typical acidic texturing process can be taken: Assuming an average industrial bath operating time of around 80h, the amount of dosed HF and $HNO_3$ during that time period accumulates to a factor of 10 to 15 higher than the original amount of HF and $HNO_3$ used for the fresh bath make-up. These figures demonstrate, that basically the overall process performance is mainly driven by an accurate dosing of the consumed chemicals and therefore their exact determination is of great importance.

To focus on controlling and characterizing wet chemical texturing processes, not only chemical information about the composition of the etching bath is important, but also structural information about the resulting surfaces (reflectance, feature homogeneity and sizes) as well as information about the resulting electrical quality of the surface. Fig. 2 summarizes the different measurement categories which are necessary to qualify a resulting surface texture. To ensure fast and nearly online detection of the chemical components of the etching bath, preferably spectroscopical measurement techniques should be applied [9], but also inline measurement capable ion chromatography systems might be used [10].

For optical analysis of the textured surfaces, mainly information about the reflectance reduction and the homogeneity of texture (coverage and feature sizes) are valuable for process analysis.
Electrical analysis involves either lifetime measurements of the textured surfaces (typically only local information) or camera-based analysis techniques like photoluminescence imaging or Carrier Density Imaging (CDI) [11, 12].

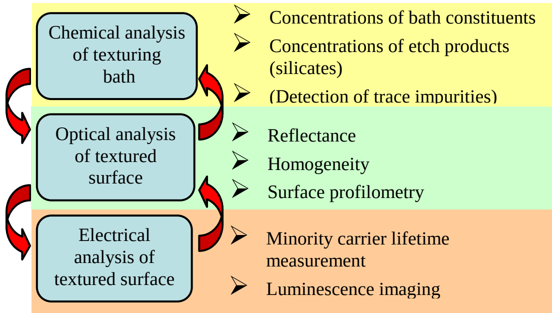


**Figure 2:** Overview of measurement categories for complete analysis of wet chemically textured silicon surfaces. The different techniques can be carried out either by means of inline or offline measurement tools.

Within the next paragraphs, application examples of the different measurement techniques and subsequent evaluation of the data is presented. Main focus has been laid on the texturing processes.

## 4 APPLICATION EXAMPLES

### 4.1 Acidic texturisation

Acidic texturisation as an isotropic process does not depend on the crystallographic orientation and hence is most suitable for multicrystalline silicon. Typically, a solution of HF, $HNO_3$ and water is used on industrial scale either in batch or inline type production equipment [13]. For the more common inline application, the wafers are moving horizontally on rolls through different tanks. A typical sequence involves the texturing itself, lowly concentrated KOH for porous silicon removal, HCl and HF clean and air drying [14]. In between the chemical treatments spray rinses are used to minimize cross contamination and to stop chemical reactions. The solar cell efficiency is strongly dependent on the etching depth of the acidic texture. If the etching depth is too shallow, crystal defects remain and the open-circuit voltage as well as the short-circuit current is reduced. If the etching depth is too deep, the surface roughness increases decreasing the open-circuit voltage and short-circuit current. This behaviour is demonstrated in Figure 3, where three different texture qualities have been applied to standard mc-Si material (size 156x156 mm², $\rho$ = 0.5 – 2 $\Omega$cm, thickness 210 µm) and final solar cells have been processed (including $POCl_3$ tube diffusion, PSG etch, Sputter-$SiN_x$ deposition, screen printing, firing, laser edge isolation). The texture varied in terms of surface roughness, texture 1 exhibits only a light texture, texture 2 represents optimum conditions and finally for texture 3, an aggressive etching solution leading to preferential etching at grain boundaries and crystal defects was chosen. The same surface effects could be observed by choosing different qualities of source material. In case of the lightly textured surface, highest shunt resistance values but also highest weighted reflectances are reached, indicating a more polished etched surface structure and sufficient $SiN_x$ homogeneity.

In comparison, texture 3 shows lowest reflectances, but also low shunt resistances and hence low $V_{oc}$. This can be attributed to an extremely rough surface structures with a lot of deep etch pits formed at crystal defects and grain boundaries. Subsequent $SiN_x$ deposition fails to homogeneously cover these deeply etched areas resulting in inhomogeneous contact formation and hence low shunt resistances and conversion efficiencies.

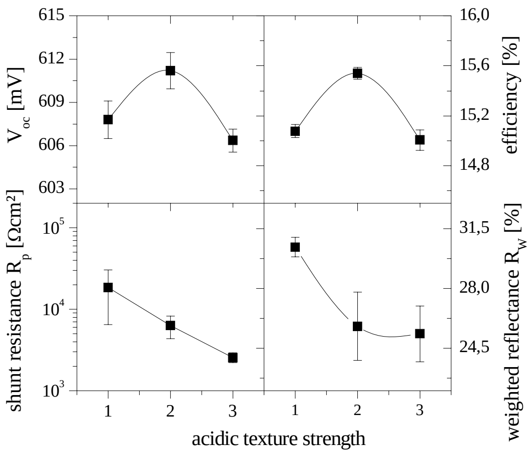


**Figure 3:** Electrical and optical results of differently textured mc-Si solar cells with subsequent industrial screen-printed based solar cell process. Texture variation 1 was lightly textured, variation 2 represents optimum conditions and variation 3 a strongly etched surface.

Due to the significant impact of the texturing result on the solar cell performance, it will be very important not only to chemically control the texturing bath, but also to optically and electrically analyze the resulting textured surface. Electroluminescence (EL) imaging represents a very elegant and fast technique to determine dislocation densities of as-cut wafers prior to as well as after the texturing process. Even simple optical scanning of the wafer after the texturing process can help to verify acidic texturing processes (Figure 4).

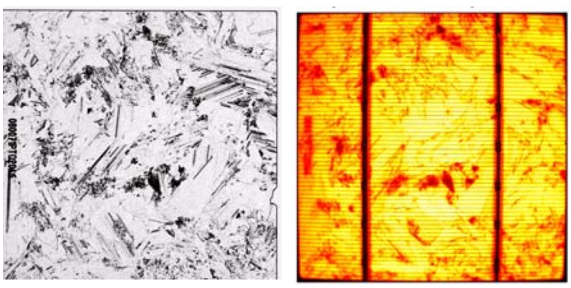

**Figure 4:** Optical and electroluminescence (EL) analysis of acidic textured mc-Si wafer: Scanned and further processed image of mc-Si wafer (left picture) and corresponding photoluminescence image (right picture). Areas with strong etch attack correspond to areas with low voltage potential (dark areas within EL picture).

In terms of process control, the coupling of chemical analysis of the bath constituents and optical and electrical analysis of the textured surface should result in a control loop, with a fast adaptation of the texturing process for varying incoming material qualities.

## 4.2 Alkaline texturisation

Alkaline etching with sodium hydroxide (NaOH) or potassium hydroxide (KOH) has different etch rates for different crystallographic orientations, hence this anisotropy results in small pyramids with a square base randomly distributed over the wafer surface for monocrystalline silicon wafers with (100) orientation [15]. To improve the lateral uniformity and the anisotropy of the etching process, isopropyl alcohol (IPA) is added to the etching solution. After texturing the wafers are typically cleaned in hydrochloric (HCl) and hydrofluoric (HF) acid with intermediate rinsing in DI water. Alkaline texturing is typically performed within batch processes, where wafers are held in carriers that allow chemicals to wet the entire surface. For standard process control, the carriers are weighed before and after etching to determine an average etching depth. Typical process temperatures range between 70 and 80°C which is close to the boiling point of the isopropyl alcohol (82°C). Constant evaporation of IPA during the etching process can be observed, which represents a major process uncertainty and results in the need for regular redosing. In order to (1) simplify the redosing of the additive and to (2) get a higher reproducibility of the initial IPA concentration it should be measured and controlled. This might be achieved by high performance liquid chromatography (HPLC) as a direct method or surface tension as an indirect method (Figure 5) [20]. IPA is surface active and lowers the surface tension of a solution. As IPA is redosed frequently a constant IPA concentration of the texturing bath could be reached.

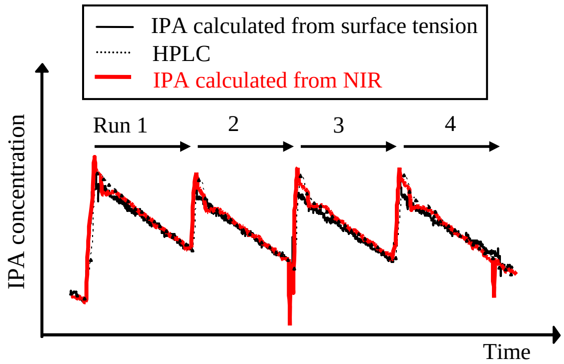


**Figure 5:** IPA concentration analysed by HPLC and IPA concentration calculated from surface tension and NIR in alkaline texturing solution with regular IPA dosing

For characterization of resulting alkaline textured surfaces, mainly the homogeneity, e.g. the area coverage of the random pyramids is of major interest. There is a clear dependence of the resulting weighted reflectance with the area coverage, as can be seen in Figure 6. The coverage is determined by means of microscope imaging. By carefully adjusting the black/white contrast of the pictures, areas with pyramids can be distinguished from areas with no pyramid coverage. The area coverage as measure for the homogeneity together with the reflectance measurement results in a sufficient optical quality control of the alkaline texturing process, both methods can be applied as spot test also with inline measurement methods.

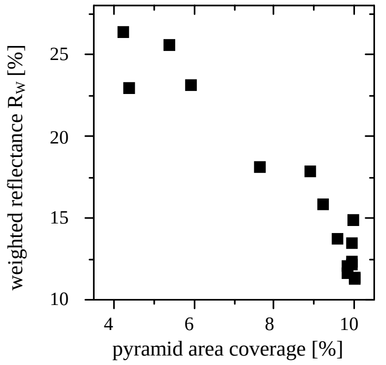


**Figure 6:** Dependence of the weighted reflectance of the alkaline textured surface with the area coverage of pyramids.

## 5 ADVANCED CLEANING PROCESSES

Various promising cell concepts from research and development are under investigation for commercialization. However, only a few more advanced solar cell technologies have already been introduced to industrial production. A big technological issue within these high efficiency approaches represents the preparation of the wafer surfaces prior to passivation steps. A clean surface is substantial for oxidation as well as dielectric layer passivation or else surface contaminants might diffuse into the bulk during subsequent high temperature steps. Shallow layers of crystal damage due to prior etching steps decrease the latter passivation quality significantly. Additionally, surfaces of industrial solar cells are, in contrast to microelectronics, generally rough due to the anisotropic damage etch or texturing processes. It is important to investigate whether a rough surface structure limits the optical and electrical performance compared to smooth shiny etched surfaces [16].

Besides these more fundamental questions of surface cleaning treatments, there is the need for transferring highly efficient cleaning sequences to industrial applications. In recent publications, different wet chemical solutions and sequences have been compared in terms of their cleaning efficiencies prior to oxidation [17] or PECVD surface passivation processes [18]. Within this paper, a standard RCA process sequence (see Figure 7) known from microelectronics was sequentially modified and simplified.

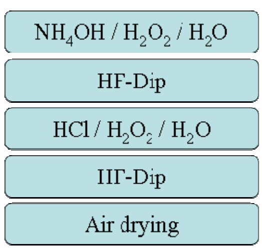


**Figure 7:** RCA cleaning sequence used within this study for surface cleaning, all steps have been performed on a large industrial wet etch system.

The simplification was done by further diluting the cleaning mixtures with DI water and the effect on the resulting cleaning efficiency was measured.

Resulting effective carrier lifetime as cleaning measure has been determined by means of quasi steady state photoconductance (QSSPC) technique at an injection level of $\Delta n = 1*10^{14}$ $cm^{-3}$. Shiny etched Fz- and KOH saw damage etched Cz-Si test wafers (p-type Fz-Si wafer, 1 Ωcm, thickness 250 µm; p-type Cz-Si wafer 1-3 Ωcm, thickness 200 µm) were cleaned and subsequent double-side deposited with a PECVD amorphous silicon layer. As a result, the dilution leads to a constant decrease of the measured lifetime on both material types (see Figure 8), numbers are given here as absolute change compared to a laboratory type hot $HNO_3$ + HF-dip cleaning sequence. Therefore a trade-off between cleaning potential and latter cell efficiency improvement or loss and total process costs has to be performed.

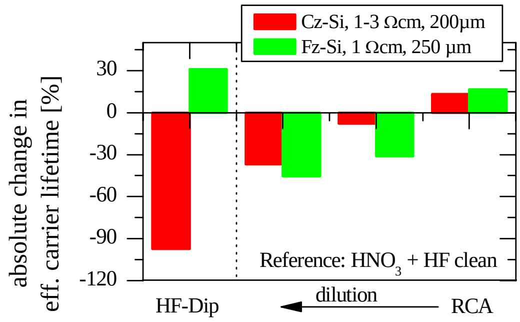


**Figure 8:** Cleaning process investigation with subsequent amorphous silicon deposition on symmetrically processed lifetime test samples (p-type Fz-Si wafer, 1 Ωcm, thickness 250 µm; p-type Cz-Si wafer 1-3 Ωcm, thickness 200 µm). The lifetime change is normalized to a $HNO_3$ + HF clean.

## 6 CONCLUSION AND OUTLOOK

Current state-of-the-art wet chemical processes are presented and future needs for a more elaborate quality assurance and process control are motivated. Especially inline or online based chemical characterization techniques are of great importance, as they allow constant and short feedback loops with the processes itself, e.g. by fast adjustment of dosing parameters. For a full characterization of texturing processes, not only the chemical information of the texturing bath is important, but also the optical and electrical quality of the textured surface. Different inline capable characterization techniques have been presented for investigation of the surface morphology, further research and development will be necessary to correlate these optical and electrical information with the chemical composition of the texturing bath.

For advanced cleaning purposes in high efficiency processing, the target for PV should be the step-by-step simplification of common cleaning sequences used in laboratory wet benches towards a single step, highly efficient surface cleaning [19].

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