Surface modification for efficiency improvement of inline solar cell manufacture

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This article first appeared in *Photovoltaics International* journal's second edition in November 2008.

ABSTRACT

Inline processing, one of the fastest-growing production processes for crystalline silicon solar cells, uses continuously operated belt furnaces to achieve higher overall throughput compared with traditional batch processing. A second, major advantage of inline processing is improved manufacturing yields through reduced breakage of today's thinner, increasingly delicate wafers. This is accomplished by eliminating several handling steps unique to batch processing techniques. This paper describes the influence of ECN-Clean, as developed by Mallinckrodt Baker and ECN in 2006, whose application increases the efficiency of solar cells produced using inline processing by approximately 0.3 percent absolute, compared with standard inline processing. The increase is achieved by using a wet chemical surface modifier after emitter formation. Additionally, experimental data is presented on establishing a stable process on an industrial scale, prior to optimization of the line for cell efficiency.

Introduction

One of the main challenges facing the photovoltaic industry in the coming years will be the reduction of the cost/Wp. One of the most effective methods available to reduce cost/Wp is to use thinner crystalline wafers. Currently, in batch systems, such as $POCl_3$ diffusion, wafers are placed vertically in a boat, entering and exiting the furnace through the same opening. This entails a great deal of handling of very fragile material, significantly raising the risk of breakage and lowering overall manufacturing yields. Current equipment is capable of handling wafers with thicknesses down to 150 micrometers. If the thickness of the wafers is reduced further, as industry roadmaps predict, increased breakage due to handling, as well as effects due to fast cooling, will become serious problems.

Inline diffusion offers a definite advantage over batch systems, in that wafer handling is minimal, and overall throughput is considerably higher than for similar batch processes. As such, the inline process is considered to be one of the most promising alternatives for high-yield cell manufacturing. Instead of using a gas-phase process to deposit the emitter source, the phosphorous is deposited onto the wafer using an ultrasonic spray or spin tool. Phosphoric acid, either in pure form

	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF (%)	Eff. (%)	J x V (mAV/cm^2)
ECN-Clean	33.3	608	77.1	15.63	20.26
No Clean	32.9	603	77.3	15.37	19.88
Diff. Abs.	0.4	5	-0.2	0.26	0.38
Diff %	1.1 %	0.80 %	-0.25 %	1.7 %	1.89 %

Table 1. Cell-level results of ECN-Clean-processed wafers. Experiments were performed on 19 neighboring wafers per group.

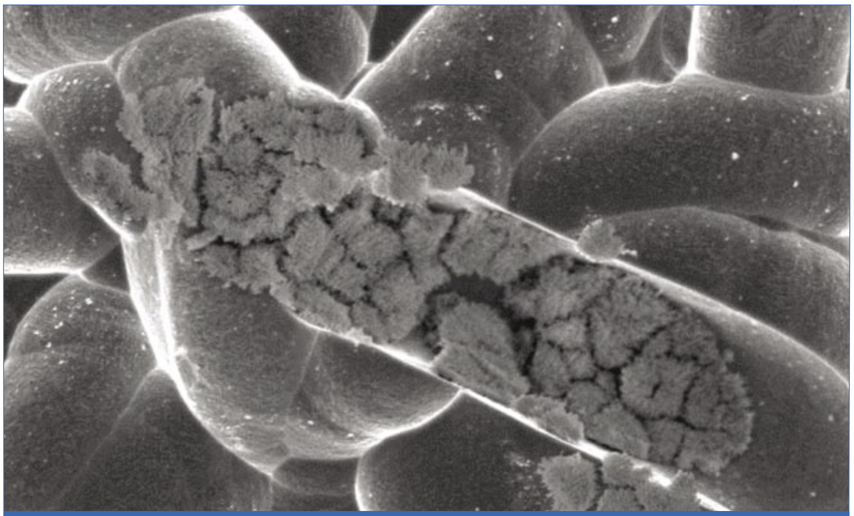


Figure 1. SEM of PSG on a textured multicrystalline wafer. PSG is visible as crystalline material. Image is 10 x 7µm.

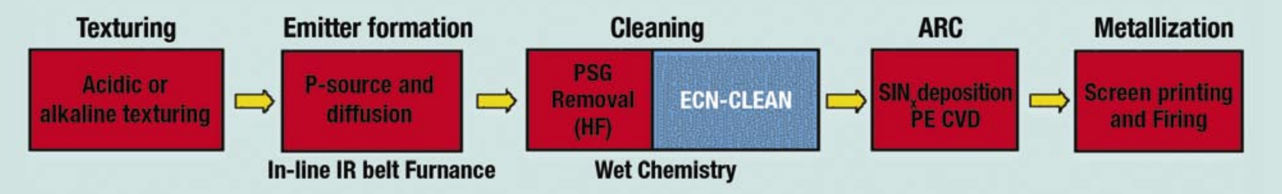


Figure 2. Schematic overview of a cell manufacturing process, including ECN-Clean.

or mixed with water, is typically used as the phosphor source for the emitter. In some cases, additives can be used to facilitate wetting of the phosphor source and to improve emitter homogeneity. The ECN-Clean is capable of increasing the efficiency of inline-produced wafers by 0.3% absolute [1,2]. Process conditions can be easily stabilized in an industrial production line prior to efficiency optimization.

ECN-Clean

In the standard cell manufacturing process, emitter formation is followed by an HF dip to remove phosphosilicate glass (PSG, or phosglass, see Figure 1), after which the passivation layer (usually silicon nitride: SiN_x:H or silicon oxide) is applied. This crucial step reduces the amount of surface recombination of charge carriers, substantially increasing short-circuit current and thereby the efficiency of the cell. To further improve surface passivation in solar cell processing, a cleaning step can be employed immediately following the PSG removal.

Traditionally, cleans like RCA1 and RCA2 are used for surface cleaning. These cleans, consisting of an etching alkaline bath and an acidic dip, have been used in the IC industry for decades. Unfortunately, these cleans involve a two-step process (excluding rinsing) at very high temperatures. ECN-

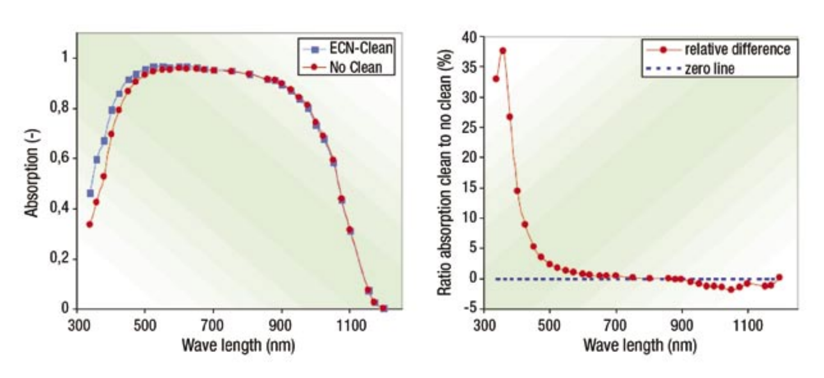


Figure 3. Plot of the absorption of incident light for ECN-Clean versus no clean, and the ratio of the two respective measurements.

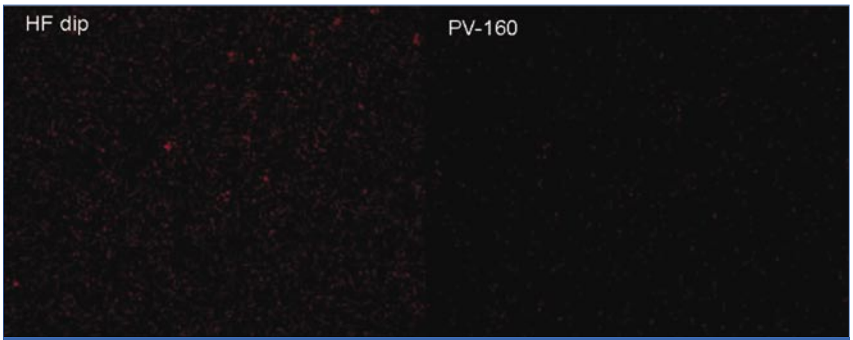


Figure 4. SEM/EDX micrographs of identical spots on a multicrystalline wafer before and after application of the BakerClean Surface Cleaner. Presence of phosphorous is indicated in red. Images are 50 x 30µm.

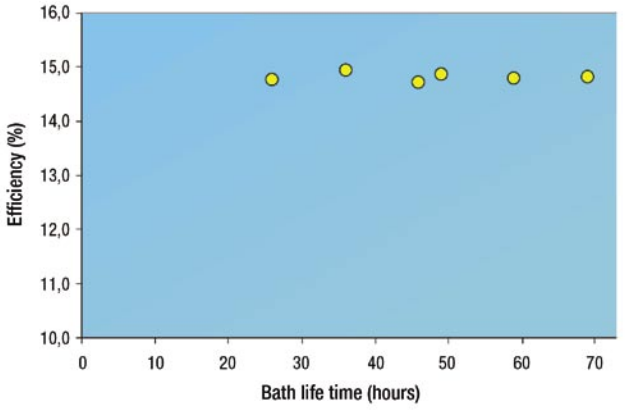


Figure 5. Cell efficiency as a function of run time for industrial production involving ECN-Clean. The purpose of the experiment was to achieve a stable line, not to optimize cell efficiency.

Clean involves applying a simple wet bench single cleaning step after standard glass removal with HF but before SiN_x:H deposition (Figure 2) [1,2].

Laboratory experiments have shown that improvements in efficiency resulting from the cleaning step were due to an increase in voltage and current, while the loss in fill factor was small (Table 1). This increase was found to be irrespective of wafer position in the ingot [1,2]. In contrast, applying a standard RCA clean resulted in a dramatic loss of fill factor of several percent, drastically reducing final cell efficiency [3].

The application of Mallinckrodt Baker and ECN's BakerClean PV-160 Solar Cell Surface Cleaner resulted in an increased blue response from the cell, as shown by IQE measurements (Figure 3).

The increased blue response is generally seen as an indication of the removal of phosphorous from the n^{++} region of the wafer [4]. In this region, the phosphorous concentration easily exceeds its solubility limit in silicon, resulting in additional charge carrier recombination near the surface. Using SEM/EDX, which is capable of determining the surface concentration of various elements, we were able to show that the application of the cleaner selectively reduces the surface concentration of phosphorous on the wafer surface (Figure 4). This results in less recombination, and leads to an increase of over 1 percent in the current. Additionally, the open-circuit voltage was found to increase by almost 1 percent, which can be attributed to the partial removal of the dead layer.

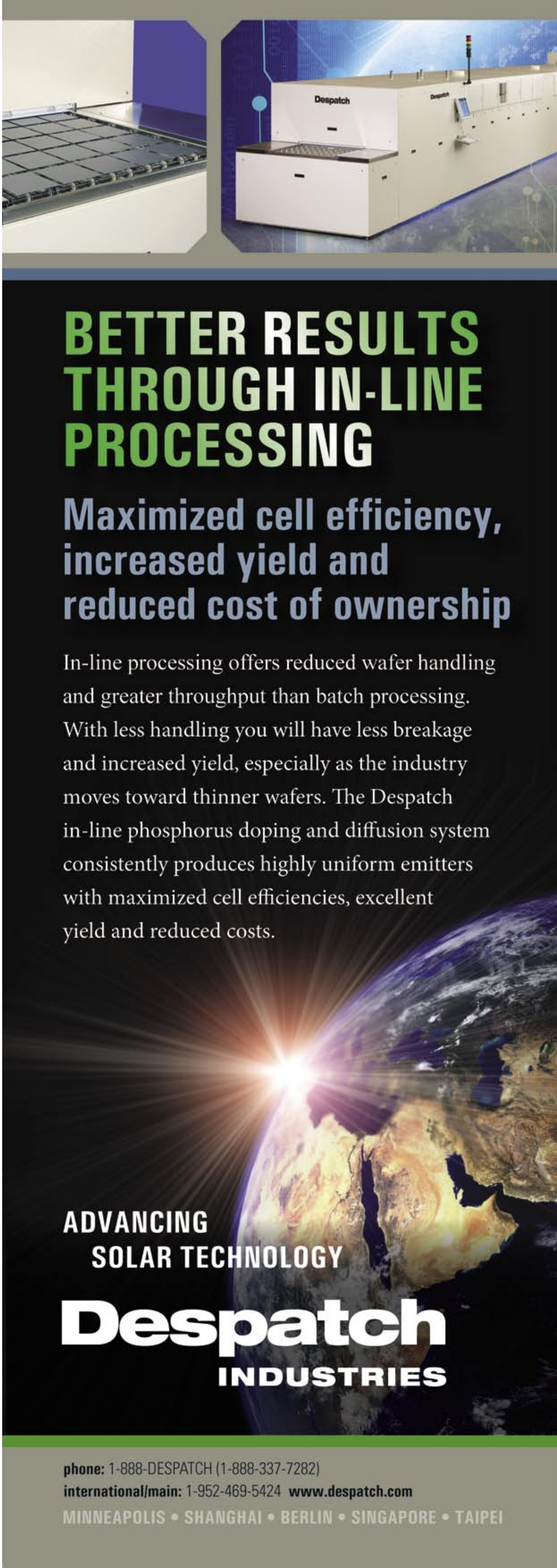
Industrial application

Translating an etching step from a simple wet bench under laboratory conditions to a fully ramped production site can be a time-consuming and costly undertaking, as it entails executing start-up protocols, on-site training of engineers and possibly down-time of the production facility.

By using a tailor-made start-up protocol, the cleaning process was implemented on an industrial production line of crystalline wafers with a spray-on phosphorous emitter. The purpose of this ramp-up procedure was to achieve stable production. At this point, the fabrication line was not yet optimized for cell efficiency.

In a 70-hour production run time, consisting of 85,000 wafers, cell efficiency and other cell parameters were monitored as a function of time. The data clearly show that all cell parameters are stable within this interval (see both Figure 5 and Table 2).

The bath conditions can be monitored both inline and offline. For this production run, several parameters were monitored in time; total bath volume and pH are shown in Figures 6 and 7. Figure 6 shows the total bath volume as a function of time. Using a tailored spiking protocol, calculated from specific equipment properties and factory conditions, the bath volume was kept within 5 percent of its initial capacity. When the spiking protocol was stopped at 58 hours, a rapid decrease in bath volume was observed due to the evaporation of water.



Time	JSC (mA/cm2)	VOC (V)	FF	Eff. (%)
26 hrs	33.00	0.601	0.744	14.8
36 hrs	33.07	0.600	0.751	14.9
46 hrs	33.03	0.599	0.743	14.7
49 hrs	33.03	0.601	0.752	14.9
59 hrs	33.02	0.600	0.747	14.8
69 hrs	32.99	0.599	0.748	14.8

Table 2. Selected cell parameters as a function of time for an industrial production run involving ECN-Clean.

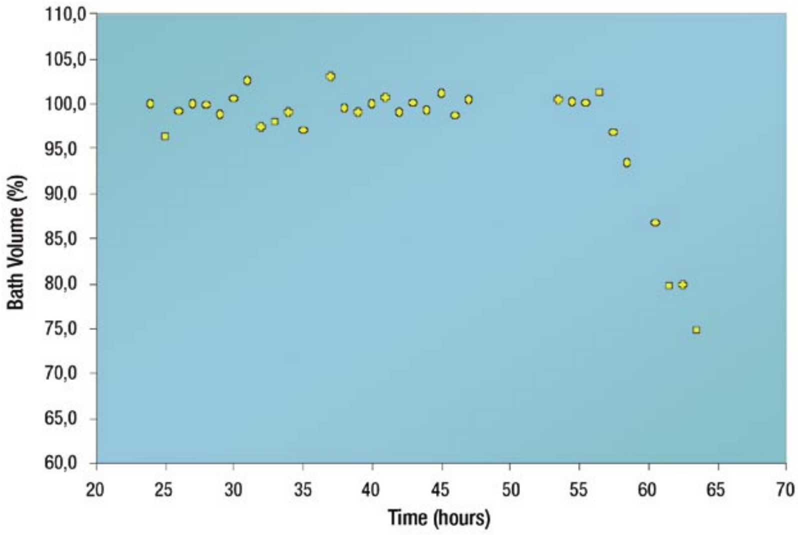


Figure 6. Plot of total bath volume as a function of time. A tailor-made spiking protocol was used to keep production conditions constant. Spiking was discontinued at 58 hours.

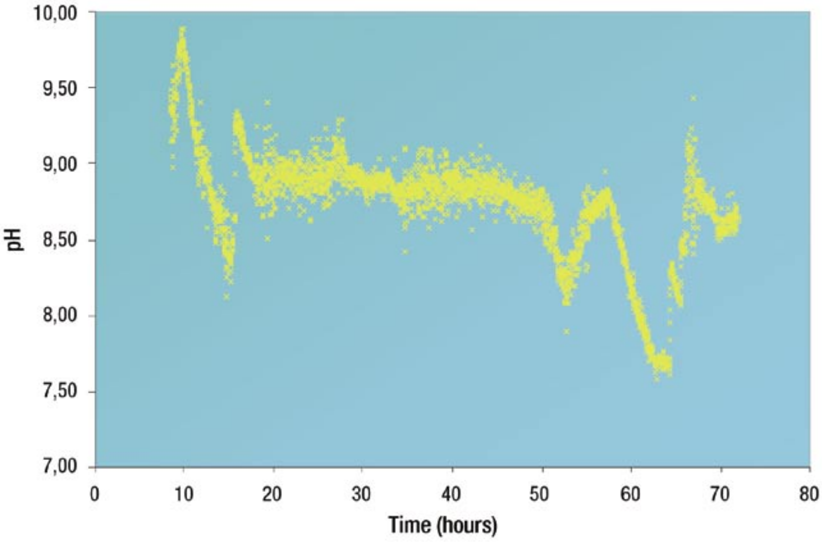


Figure 7. Plot of pH of the ECN-Clean bath during the production run. The stable regime was achieved with a tailor-made spiking protocol.

Other parameters, such as the concentrations of the individual components of the ECN-Clean, were also monitored. These components were stable up to the discontinuation of spiking, similar behaviour to that displayed by the total bath volume.

The pH was measured inline at normal operating temperatures. By tailoring the spiking protocol, we were able to keep the pH stable during the production time, up to discontinuation of spiking (Figure 7). The initial fluctuations in the pH value were attributed to discontinuation of temperature control and the cessation of spiking, after having heated the bath to its operating temperature, to observe what effect this would have on the properties of the bath. As expected, bath volume decreased during this time and the concentration of the individual components fluctuated (not shown), as did the pH. Once temperature and spiking control were reinstated, at 15 hours, the pH returned to stable values up until spiking was stopped. At 65 hours, the spiking protocol was reinstated, which once again resulted in a stable pH of the bath (Figure 7).

These experiments show the importance of tailored spiking in achieving a stable, running production line.

Conclusion

This paper presents data on the ECN-Clean process, which was designed to selectively etch excess phosphorous from inline emitters, thereby increasing the blue response of the cells. This controlled post-emitter etch increases the current and voltage of the solar cells by about 1 percent, resulting in an efficiency increase of 0.3 percent absolute, independent of wafer quality. Additionally, an industrial example of the application of this process is shown, resulting in a stable production line before efficiency optimization. The data show that by using a tailor-made start-up protocol, a stable production run of 70 hours and 85,000 wafers was achieved.

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About the Authors

Johan Hoogboom obtained his doctorate in physical-organic chemistry and solid-state physics from the Radboud University in Nijmegen, The Netherlands, in 2004. His studies focused on self-assembled alignment layers for LCDs. Hoogboom then moved to the Massachusetts Institute of Technology as a postdoctoral fellow, working on polymer-based explosives sensors in a joint project with the U.S. Army. In 2006, he returned to the Radboud University as an assistant professor in organic electronics, coordinating material research into organic solar cells, LEDs, FETs, TFTs and nanowires. In 2008, Hoogboom joined Mallinckrodt Baker where he is the global R&D coordinator for silicon photovoltaics.

Luuk Groenewoud obtained his doctorate from Twente University in Enschede, The Netherlands, in 2000, focusing on the vapor deposition of conducting polymers. After a stint at Holland Biomaterials Group in Ensched e, where he developed stents and other biocompatible surgical components, Groenewoud joined Mallinckrodt Baker as R&D manager in 2005. Currently, Groenewoud heads a research group at the Advanced Technology Centre of Philips in Drachten, The Netherlands.

Jan Oosterholt studied Analytical Chemistry at the Rijkshogeschool IJsselland in Deventer, The Netherlands. In 1998, he obtained his bachelor's degree with a final internship at the Akzo Nobel Central Research Centre in Deventer on Capillary Electro Chromatography (CEC). Oosterholt started working in Mallinckrodt Baker's Quality Control department, where he obtained experience in analytical chemistry. In 2003, Oosterholt moved to Mallinckrodt Baker's R&D department as a research chemist where he now supports the PV team with his analytical knowledge as a Senior Chemist.

Dr. Jan H. Bultman has been one of the group leaders of Energy research Centre of the Netherlands' (ECN) Crystalline Silicon PV technology group since 2003. He is responsible for industry projects, technology transfer and finances. In 2002, Bultman was responsible for the acquisition of the Integrated Project Crystal Clear together with Paul Wyers. In 1998, he started the development of the Pin-Up Module, now one of the main areas of PV research at ECN. Since 2000, Bultman has been involved in knowledge transfer between ECN and industry, acquiring and negotiating license agreements with numerous industrial entities. Bultman studied Physics and obtained a doctorate in Nuclear Engineering at the Technical University Delft.

C. (Kees) J.J. Tool, M.Sc. is a chemist by education. As project member of the Topsicle project he was a key contributor responsible for the realization of the 17.0 percent efficient solar cell. Tool has been responsible for the stability and development of the ECN baseline process for several years. As senior research scientist and project leader of industrial projects he is responsible for the implementation of this ECN process in turnkey production lines and for support of industrial partners to improve their production lines.

Dr. Arno Stassen has worked as a research scientist in ECN's Crystalline Silicon PV Technology group since 2006, addressing chemical etching, oxidation and cleaning of silicon wafers. He is also involved in knowledge transfer of chemical processes to the industry. Dr. Stassen studied chemistry at the Radboud University Nijmegen and obtained his doctorate at Leiden University in 2002. From 2002 to 2006, he worked as a post-doctoral research fellow in chemistry at the Technical University of Vienna and Leiden University, and in applied physics at the Technical University of Delft and the ETH Zürich.

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