

# Removal of trace metals using a biodegradable complexing agent

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## ABSTRACT

Processing silicon substrates for PV applications involves texturing, cleaning and/or etching wafer surfaces with chemical solutions. Depending on the cleanliness of the industrial equipment and the purity of the chemical solutions, surface contamination with metals or organic residues is possible [1]. The presence of trace contamination at PV junctions leads to both mid-level traps and photonic defects, which ultimately cause reduced efficiency and rapid cell degradation. Metallic impurities have a greater impact on PV cell lifetime due to their deeper energy levels in the silicon band gap [2]. On the other hand, non-metallic impurities may modify the electrical activity of PV cells because these species involve complex interactions with the host silicon lattice and its structural defects. In other words, very small amounts of contamination can result in poor PV efficiency. This paper presents an overview of the effects of adding a biodegradable complexing agent in cleaning and rinsing baths to minimize surface contamination and thereby enhance solar cell efficiency.

## Introduction

Conventional approaches in the solar industry for cleaning silicon have historically used either standard equipment and/or chemicals derived from semiconductor processing [3, 4]. These approaches, although effective in deep submicron processing common in semiconductor technologies, can be both dramatically over-engineered and ineffective for PV processing due to the inherent differences between solar cells and microelectronic devices. An effective approach to remove metal contamination during solar cell processing could aid manufacturers in meeting or exceeding solar cell efficiency and performance goals.

## Standard wet chemical processes in industrial cell processing

Several wet chemical process steps, including surface preparation prior

to junction diffusion and oxide etching following diffusion, are critical components of the silicon solar cell manufacturing sequence. Table 1 provides an overview of currently used wet chemical etching and cleaning steps within the front-end of a standard production sequence for c-Si solar cells based on screen printing.

Pre-cleaning of wafers, prior to texturing, is gaining importance due to the removal of organic residuals and metallic contamination from the wafering step which improves the homogeneity of the subsequent texturing step. Mostly alkaline cleaning solutions are utilized for texturing single crystalline wafers. These are similar to the common SC1 (standard clean 1 - NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>), known from semiconductor processing [5]. Texturing of multicrystalline wafers takes advantage of wafer saw damage in an aqueous acidic etch utilizing a combination of HNO<sub>3</sub> to

oxidize the wafer and HF to etch the oxide. Significant metal contamination can build up in these baths as the bulk of the wafer is etched away [6].

Prior to emitter diffusion, any remaining alkali metal contaminants from the single crystal texturing process are removed by a second, additional cleaning step. Further on in the process, especially for subsequent inline diffusion processes, where e.g., diluted phosphoric acid or phosphoxychloride (POCl<sub>3</sub>) is deposited on the wafer, the cleaning step also acts as a 'conditioner' to create a hydrophilic wafer surface. This ensures sufficient wetting of the wafer with the phosphoric acid. Therefore, HCl and HF 'dips' are used for the cleaning after texturing, and the surface is made hydrophilic by applying either gaseous ozone or rinsing with ozonated DI water [7].

During emitter diffusion a thick layer of a phosphorous silicate glass (PSG) is created on the wafer surface. This PSG layer can contain a significant concentration of metallic impurities that have been 'gettered' from the wafer bulk as the metallic contaminants can segregate preferentially into this layer. It is important that during the removal of the PSG, metals which are liberated from this layer do not redeposit on the wafer surface from the bath. For additional surface preparation prior to SiN<sub>x</sub> antireflection coating, ECN developed a specialized, highly alkaline, not biodegradable selective etching mixture (commercial products are nowadays available from companies like Avantor or BASF), which removes the highly P-concentrated top surface emitter layer (so-called 'dead layer') especially observed after inline diffusion processes [8]. Similar performance levels can also be obtained using the already mentioned

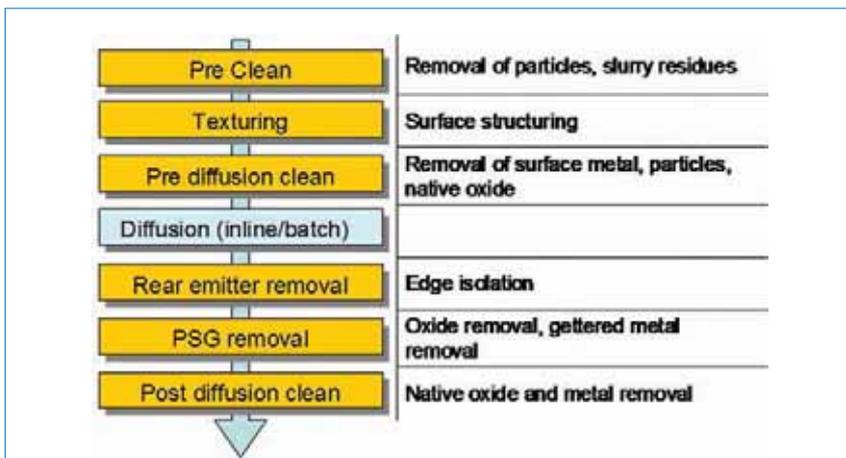


Table 1. Overview of currently used wet chemical etching and cleaning steps within the front-end of a standard production sequence for c-si solar cells.

SC1 mixture or HF/ozone treatments. This removal results in a better blue response and typically slightly higher  $V_{oc}$  and  $J_{sc}$  values of the final solar cells. The process is not a drop-in replacement of current cleans; it requires a separate step, which means additional capital equipment cost.

Depending on the industrial equipment or purity of chemicals used, contamination of the surface with metals or organic residues is possible. Reduced efficiency and rapid cell degradation share common roots, being trace contamination at the photovoltaic junctions leading to both mid-level traps and photonic defects. The extremely high fields that exist at p-n junctions during operation of the finished device can also give rise to surface migration of ionic impurities if they are not removed. The effects of these contaminants may result in uncontrolled drifts of the surface potential, changes in the minority-carrier lifetime at the surface, surface recombination velocity, and the formation of inversion or accumulation layers. These effects can lead to increased and erratic reverse leakage current in devices [2].

### Impact of metal contaminants on solar cell devices

The main issue with standard processing sequences (in production at most mc-Si and c-Si manufacturing facilities: see Table 1) is the lack of a consistent chemical method to remove Cu from wafer surfaces and cleaning baths. There are two approaches to control the electrically active impurity concentration in silicon solar cells:

- 1) Minimize contamination of the silicon base material by purification to provide the highest value of diffusion length possible in the wafers from which cells are made; and
- 2) Maintain or improve the initial diffusion length by chemical or thermochemical impurity 'gettering' techniques during the cell processing itself.

In the first method, the intent is to eliminate impurities; in the second, they may be removed from the device itself or made electrically inactive. In the solar cell industry, the cleaning of silicon wafers before different passivation and texturization treatments has not yet been studied intensively in detail. The most frequently used cleaning sequence is the RCA-clean (Radio Corporation of America), but the cleaning effect and the influence on solar cell parameters are not completely understood. Questions concerning the required bath purity (or loading) and subsequent silicon surface contamination can only be answered

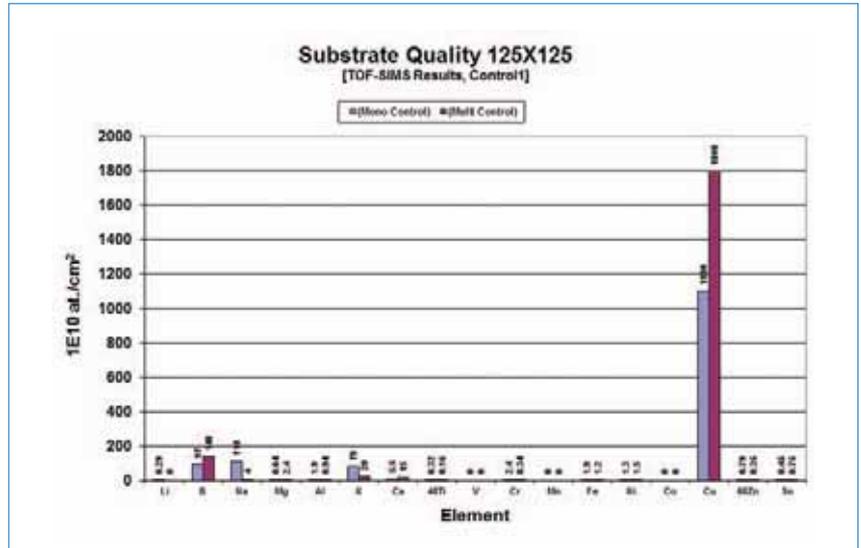


Figure 1a. As-received prime silicon substrates (mc-Si and c-Si); TOF-SIMS results.

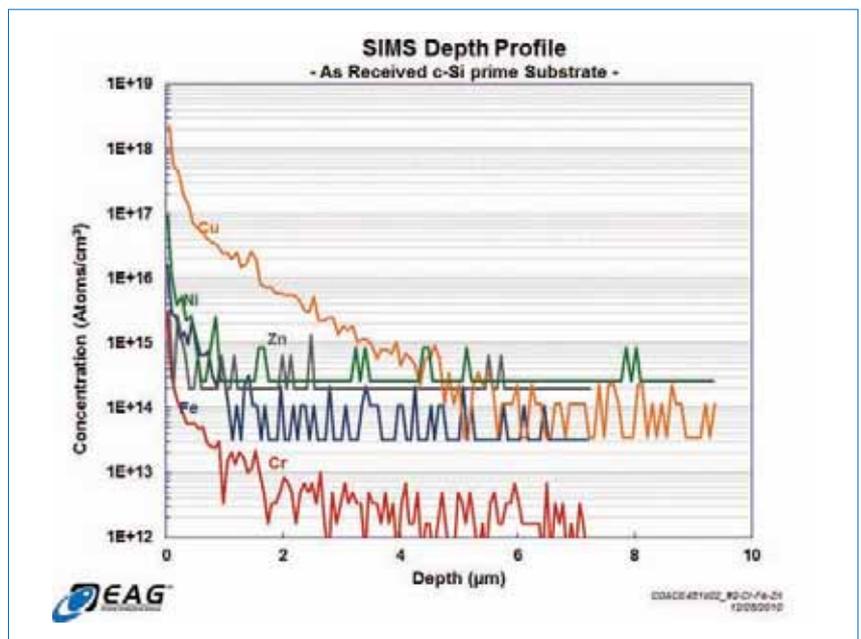


Figure 1b. SIMS depth profile of Cu, Fe, Ni, Cr and Zn; pristine c-Si substrate.

empirically. The contamination for which the Sunsonix clean (adding of a biodegradable complexing agent to aqueous cell processing solutions) has been developed, is that of metallic cations liberated from the substrate surfaces into the wet processing baths. The contamination of the substrate surfaces usually occurs as a result of physical or chemical adsorption by electrolytic action or by exchange of surface atoms with impurity ions in the cleaning solution [2]. Cu contamination is likely a result of the wafering process, since standard wires used to slice Si ingots are made of a metallic composite (e.g. a stainless steel core surrounded by a bronze or copper layer).

Time of flight secondary ion mass spectrometry (TOF-SIMS) analysis of solar-grade mc-Si and c-Si wafers detected 1.1-1.8  $\times 10^{13}$  atoms/cm<sup>2</sup> of Cu from the samples on

the surface and Dynamic SIMS (D-SIMS) analysis detected  $5 \times 10^{16}$  atoms/cm<sup>3</sup> in the bulk at 1µm depth (Fig. 1a & Fig. 1b).

All impurities were detected at the surface region. Shapes of Cr, Fe, Ni and Zn profiles are most likely sputtering artifacts caused by surface roughness. High levels of Cu were detected both at the surface and a few micrometers into the sample. Bulk detection limits for this analysis are (in atoms/cm<sup>3</sup>): Cr <  $3 \times 10^{12}$ , Fe <  $3 \times 10^{13}$ , Ni <  $2 \times 10^{14}$ , Cu <  $1 \times 10^{14}$  and Zn <  $2 \times 10^{14}$ .

### Impurity effects

Defects or dislocations in the silicon lattice are sites where recombination centres can occur. Recombination results in the loss of photo-generated carriers (e.g., electrons drop from the conduction band back into the valence band and holes do the opposite) and significantly degrades the photovoltaic quality of the device.

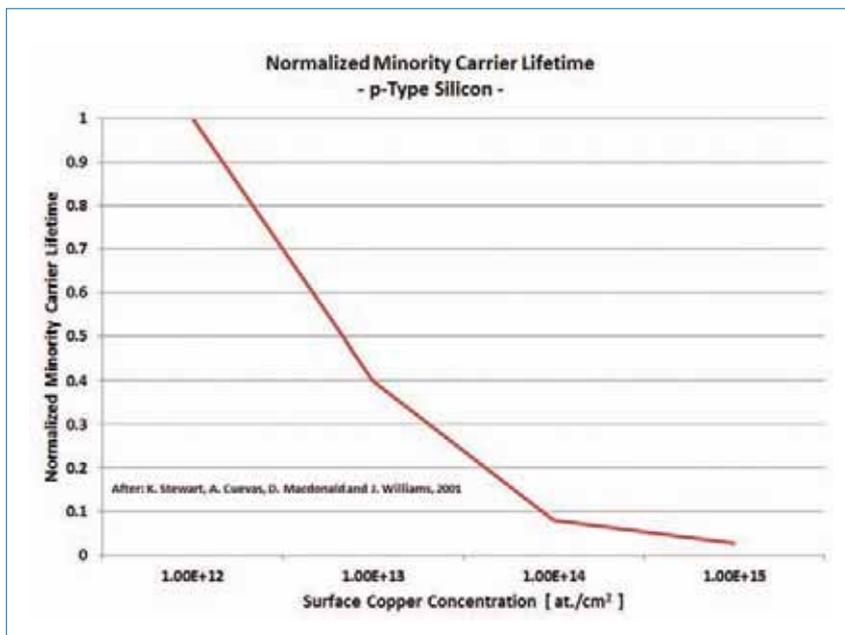


Figure 2. Impact of increasing copper contamination on the normalized minority carrier lifetime [7].

Diffusing trace metals lead to displacement damage (dislocations, stacking faults, precipitates etc.), and deep recombination centres reducing the minority carrier diffusion length. There are numerous metal species which introduce deep-level traps that stimulate the recombination of photogenerated carriers in silicon. Cu and Ni impact junction degradation, and Nb, Ti, V, Ta, W, Mo, Pd, Au, Zr, Mn, Al, and Sn, the removal of which has a great influence on carrier diffusion length reduction. Fe, Cr, Co and Ag have detrimental effects on both of these loss mechanisms. The presence of metallic impurities in the photovoltaic material is responsible for the formation of hot spots by metal agglomeration that are particularly problematic since they are responsible for creating localized increase of the electric field, inducing avalanche breakdown that leads to non-uniform current densities.

**“Copper can easily diffuse through the thickness of a solar cell within a few hours at room temperature.”**

Such effects will decrease the open-circuit voltage  $V_{oc}$ , short-circuit current density ( $J_{sc}$ ) and fill factor, which represents the relationship, or balance, between current and voltage for effective power output. Of particular interest in this paper is the near ubiquitous presence of copper in ‘solar-grade’ silicon wafers. Copper can easily diffuse through the thickness of a solar cell within a few hours at room temperature [9]. Formation of

Cu precipitates in the area of the p-n junction may shorten it and decrease the overall efficiency of the cell [4]. The carrier lifetime in Cu-contaminated Si is lower in n-type than in p-type Si (see Fig. 2) [10, 11]. Furthermore, copper diffuses in Si as a positively charged interstitial ion. The intrinsic diffusivity is  $2.4 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1}$  at room temperature. Positively charged Cu ions pair with the negatively charged acceptor atoms which tends to concentrate the copper near the depletion region of the p-n junction where the fields are enhanced. This may be one mechanism for the known degradation of crystalline silicon solar cells of about 0.5% per year.

### Analysis of trace metals during wet chemical processing of silicon wafers

We have identified why many industrial manufacturers have overlooked the influence of copper contamination on PV wafers. Standard methods of analyzing surface contamination are ICP-MS (Inductively Coupled Plasma Mass Spectrometry), ICP-AES (inductively coupled plasma atomic emission spectroscopy), and ICP-OES (inductively coupled plasma optical emission spectroscopy). These methods use an acid wash, usually based on HF or HF/HCl, of the wafer surface where it is assumed that the acid solution effectively removes all metallic contamination from the wafer surface. The solution is then concentrated and injected into the plasma of the spectrometer. In our work we determined that the standard ICP-MS solution did not effectively remove Cu and gave a false negative value for Cu concentration since metals are known to electrochemically

plate out from an HF solution onto a bare silicon surface. The direct surface measurement by techniques such as TXRF (total reflection X-ray fluorescence spectroscopy) suffer from accuracy and detection limit due to stray reflection on the rough morphology of the PV substrates. Other direct methods utilize sputtering of the sample surface to liberate analyte ions which are detected by mass spectrometric techniques. SurfaceSIMS (surface secondary ion mass spectrometry, a type of dynamic SIMS), and TOF-SIMS [16, 17] are two such methods with the detection limits required for our PV application. TOF-SIMS was chosen as the method of choice in the current study for a number of reasons:

- It can detect all of the typical metal elements of interest in survey mode without the need to pre-select species of interest.
- The information depth of the measurement is very low, typically in the 10–20Å range.
- It is not adversely affected by the potential presence of particle contamination, or sample roughness.
- It has excellent detection limits, i.e. in the  $1 \times 10^9$  at/cm<sup>2</sup> range for many transition elements, and substantially lower for alkali or alkali earth elements [16–18].
- No sample preparation is required and it is a direct analytical method, unlike VPD-ICP-MS/AAS which requires the use of appropriate chemistry and equipment to dissolve the surface of interest and concentrate it for analysis [19–22].

For the analysis performed for this work a Ga<sup>+</sup> primary ion source was operated in pulsed, bunched mode with a beam energy of 15kV and with a 20nA beam current, in order to maximize sensitivity for elemental species in the positive ion mode. The instrument conditions were optimized for high mass resolution (typically 8000 at m/z 41) and abundance sensitivity to enable the best sensitivity for elemental ions.

### Working principle of SX-E complexing agent

Over the past three years, novel, proprietary, biodegradable and biocompatible (i.e., green) cleaning chemistries and processes have been developed for the removal of detrimental trace metal contamination, e.g. from solar cell substrates during cell manufacturing processes. In testing performed by a variety of academic institutions, independent research labs,

industry equipment providers and solar cell manufacturers, this technology has been demonstrated to deliver a direct improvement of crystalline silicon (c-Si or mc-Si) absolute efficiency. The use of this type of cleaning not only enables improving and controlling the material quality, but participates actively to the process cycle by limiting the need for pre- and postdiffusion cycles aimed at getting the minority carrier lifetime killing metallic impurities. Because its use is not limited to wafer type Si-based substrates, it also offers a scalable and extendable solution for any type, size or shape of substrates and participates to increase total cell efficiency and to reduce cell lifetime degradation. These chemistries/processes can be seamlessly incorporated into existing production lines at four process steps: silicon ingot reclaim, wire saw (wafering), substrate cleaning and texturing. The target cleaning agent used in this study, SX-E, is chemically compatible with almost all standard semiconductor and PV processing sequences and chemicals.

Contamination of Si surfaces by metallic impurities from reagent solutions is particularly severe in aqueous HF which strips the protective layer of natural oxide without etching the semiconductor. The large difference between the oxidation potentials of the Si and the metal ions in solution therefore becomes effective over the entire surface leading to large quantities of electrochemically deposited metals, in particular Cu (see Fig. 1a) [2, 3].

An ideal reagent would keep the metals in solution (i.e. to dissolve metals) and prevent oxidation/reduction reactions between Si and metal ions. It has been found that oxidation/reduction reactions can be prevented by increasing the redox potential of solutions and/or by injecting surfactants or chelating agents [12].

There are four deposition mechanisms when metallic impurities contaminate the Si wafer surface in solutions:

- 1) Electrochemical deposition: metal is deposited on the surface due to an electrochemical reaction between the metal ion and Si.
- 2) Precipitation: as some of the metals form metal hydroxides in alkali solutions, their deposition is attributed to precipitation of metal hydroxides on the substrate surface.
- 3) Film inclusion: metallic impurities close to the Si surface are included into the oxide as the Si surface is chemically oxidized by oxidizing agents, such as dissolved oxygen and H<sub>2</sub>O<sub>2</sub>.
- 4) Chemisorption: weakly bonded metal hydrate or halide that can be incorporated as described in mechanism (3).

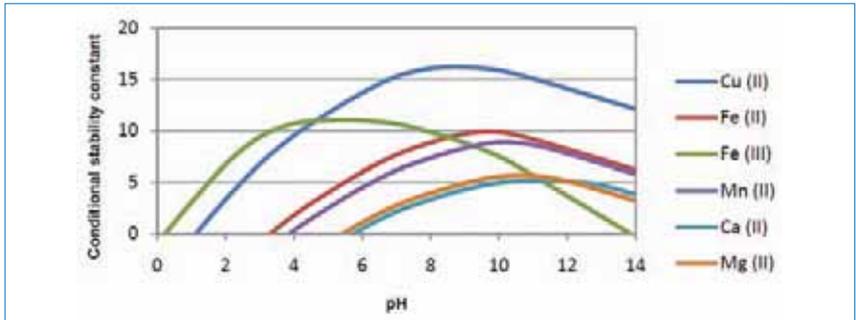


Figure 3. Conditional stability constant of the precursor for SX-E.

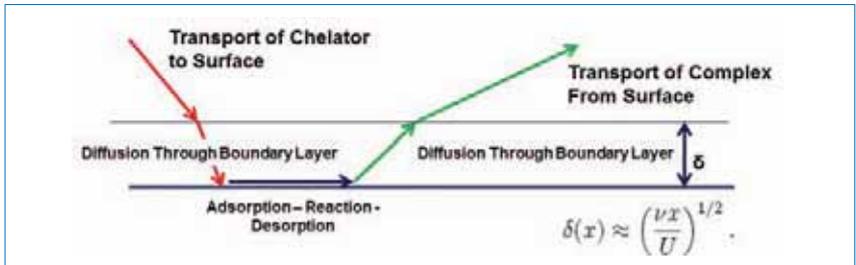


Figure 4. Metal removal by chelating agents.

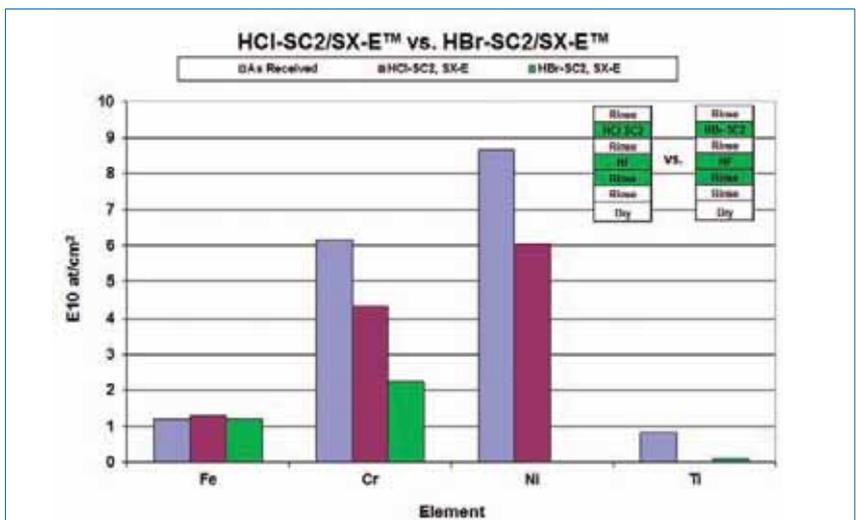


Figure 5a. Cleaning efficiency using SX-E - HCl-SC2/SX-E vs. HBr-SC2/SX-E; Fe, Cr, Ni and Ti results.

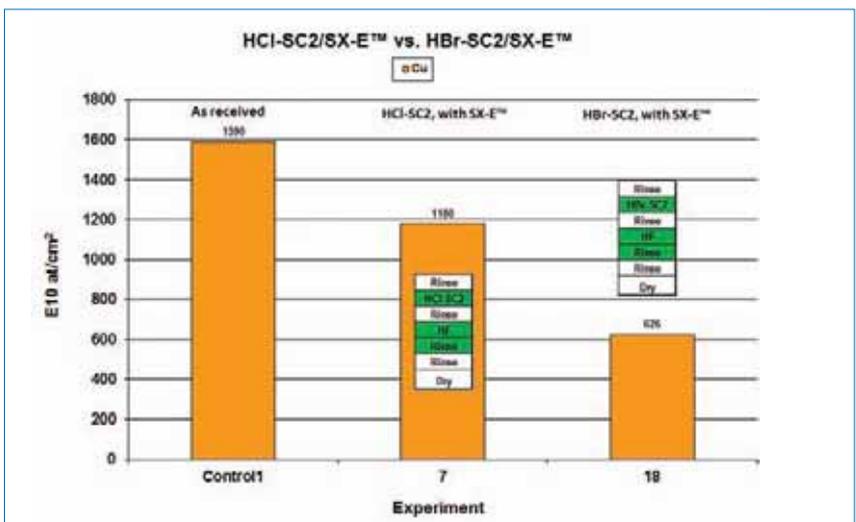


Figure 5b. Cleaning efficiency using SX-E - HCl-SC2/SX-E vs. HBr-SC2/SX-E; Cu results.

The contamination for which the SX-E clean has been developed is that of metallic cations liberated from the substrate surfaces into the wet processing baths. The contamination of the substrate surfaces usually occurs as a result of physical or chemical adsorption by electrolytic action or by exchange of surface atoms with impurity ions in the cleaning solution [2]. The unusual property of this specific cleaning agent is its ability to solvate metal ions in 1:1 metal-to-SX-E complexes. As the cleaning agent solvates the cations, the number of recombination sites is reduced and the conversion efficiency of light energy into electrical energy is augmented. If not removed, the metallic ions (positively

charged ions in silicon) in the depletion region can pose an opportunity for electron-hole recombination sites that degrade the conversion efficiency of the solar cell as explained earlier.

**“The unusual property of this specific cleaning agent is its ability to solvate metal ions in 1:1 metal-to-SX-E complexes.”**

It is common for SC2 chemistry to remove post-texturing residue. The low pH of the SC2 bath caters mostly to the removal of iron and leaves the copper

contamination at the initial level (see also Fig. 5a). The substitution of HCl in the SC2 solution by HBr is suggested (see Fig. 5a & 5b). Using HBr instead of HCl results in significant removal of all metals of interest compared to as-received values.

The fully deprotonated form (all acidic hydrogen removed) of SX-E binds to the metal ion. The equilibrium or formation constants for most metals, especially the transition metals, are very large (see Fig. 3); hence the reactions are shifted to the solvated metals.

Many of the reactions are pH-dependent. The conditional constant gives a relationship between the concentrations of the solvated complex formed (MeZ), the concentration of the unreacted metal (Me), and the concentration of the unreacted cleaning agent (Z). These constants pass for all metal complexes through a maximum as a function of the pH value [12]. At the thermo-dynamic equilibrium, the complex formation is selective. The most preferred metals being complexed are those with the highest conditional complex-forming constants. With increasing concentrations, other metal ions are complexed successively (Fig. 4). As shown in Fig. 7 and 8, the range of pH over which the SX-E precursor exhibits stability is consistent with the aqueous process steps used in PV manufacturing.

SX-E can only remove trace metals in ionic form. Therefore, the metal residuals from the wire sawing need to be oxidized in order to be removed.

### Cleaning kinetics using HBr

The copper contamination on the sawn substrates from the wafering process is largely present as copper metal. This is so by direct inspection of the electrochemical half cell reaction of either Cu(I) or Cu(II) in contact with silicon. Given the extremely high rates of copper diffusion in silicon it is not surprising that the copper is not only present on the wafer surface but also present in significant concentrations in the bulk of the wafer. In either mc-Si or c-Si the texturing process results in baths with a high loading of copper where the copper represents a significant surface contaminant.

The use of the SC2 bath (composed of HCl and peroxide or ozone) to remove critical transition elements like Fe is not as effective on Cu. It is well known in the plating industry that HBr is more effective in dissolution of Cu than HCl. The electron affinities for CuCl<sub>2</sub> and CuBr<sub>2</sub> have been determined to be identical, 4.35+/-0.05eV. Both the anions and neutral CuX<sub>2</sub> species are linear with only a slight bond length variation between the charged and neutral species [23]. However, Br<sup>-</sup> is a softer ion than Cl<sup>-</sup> in the Lewis acid base theory.

Concentrations:		Temp [°C]	Grade
HF	10:1 (5.14%)	RT	48%, Class 10 Grade
HF/H <sub>2</sub> O <sub>2</sub>	3:1:20	RT	
HCl	2.06%	RT	38%, Class 10 Grade
HBr	2.06%	RT	48%, SemiGrade, 99.5% Minimum Purity
H <sub>2</sub> O <sub>2</sub>	1.58%	RT	30%, Electronic Grade
SC2 (HCl or HBr based)	1:1:20 @ 60 deg C	60	
DIW		RT	16.84 MΩ
DIW/SX-E <sup>2-</sup>	SX-E ~ 300 ppm	30	
N <sub>2</sub> (Drying)			bottled high purity

Table 2. Chemicals used for laboratory testing.

	Fe	Cr	Ni	Ti	Cu
	Expected	Expected	Expected	Expected	Expected
Standard	↓	↔	↘	↓	↓
Test 1	↓	↓	↓	↓	↓
Test 2	↓	↓	↓	↓	↓
Test 3	↘	↓	↑	↘	↘
Test 4	↓	↓	↓	↓	↓
Test 5	↘	↓	↗	↓	↓

Table 3. Expected trends of cleaning chemistry impact on trace metal removal. Every line constitutes a cleaning sequence with one step changed; arrows 'up' are suspected to be a sign of re-plating of metal from any one of the cleaning chemistries (other than SX-E); see also [2].

	Fe	Cr	Ni	Ti	Cu
	Is	Is	Is	Is	Is
Standard	↘	↓	↓	↓	↗
Test 1	↘	↓	↓	↓	↓
Test 2	↑	↓	↓	↓	↓
Test 3	↓	↓	↓	↓	↑
Test 4	↑	↓	↓	↓	↓
Test 5	↓	↓	↓	↓	↑

Table 4. TOF-SIMS results on cleaning sequences used.

Electron affinity falls down the Group 7 elements in the periodic table. The affinity for copper on silicon follows the same trend when exposed to these acids.

CuX<sub>2</sub> species are expected to therefore complex at rates similar to those of SX-E. HBr dissolves copper quicker than HCl to form CuBr<sub>2</sub>. This reaction is in equilibrium with formation of adsorption layer of Br<sup>-</sup>. Whether this chelation occurs on the surface (before CuBr<sub>2</sub>) is solvated and leaves the surface or occurs in solution is unknown. At the operational pH and the SX-E configurations available the copper-bromide chemistry is favored. Either way, oxidation of copper metal to Cu<sup>+</sup>/Cu<sup>++</sup> appears to be rate limiting. The rate limiting difference between HCl and HBr precedes formation of CuX<sub>2</sub>. The addition of a strong oxidizer like H<sub>2</sub>O<sub>2</sub> facilitates the complete oxidation of formed Cu<sub>2</sub>O. SX-E complexes the species by making a mixed thermodynamically favoured Cu(X)SX-E complex (with higher stability when X=Br), stabilizing that intermediate against re-reaction/reduction with the silicon surface.

### Reduction of metal contamination using SX-E

#### Laboratory testing

Environmental awareness has traditionally motivated the research of renewable energy sources. The technical investigation in this phase proves that biodegradable chelating chemistry is effective in controlling trace metals on silicon surfaces. The tests simulate a standard pre-diffusion cleaning sequence and use the contamination test as a dependent response. The experiments for this portion of the technology are designed to optimize the process treatments for various factors, for example SX-E application in various steps, time in the bath, temperature, and chemicals used, for specific applications to establish the factors to achieve the optimum low trace metal level (Table 2–4; Fig. 6 & 7).

“The experiments for this portion of the technology are designed to optimize the process treatments for various factors.”

Critical success factors are expressed in the results that are obtained from the analytical chemical tests, presenting trace metal levels in atoms/cm<sup>2</sup>. All test sequences performed were compared to as-received substrates and against standard cleaning sequences used in a manufacturing environment. The

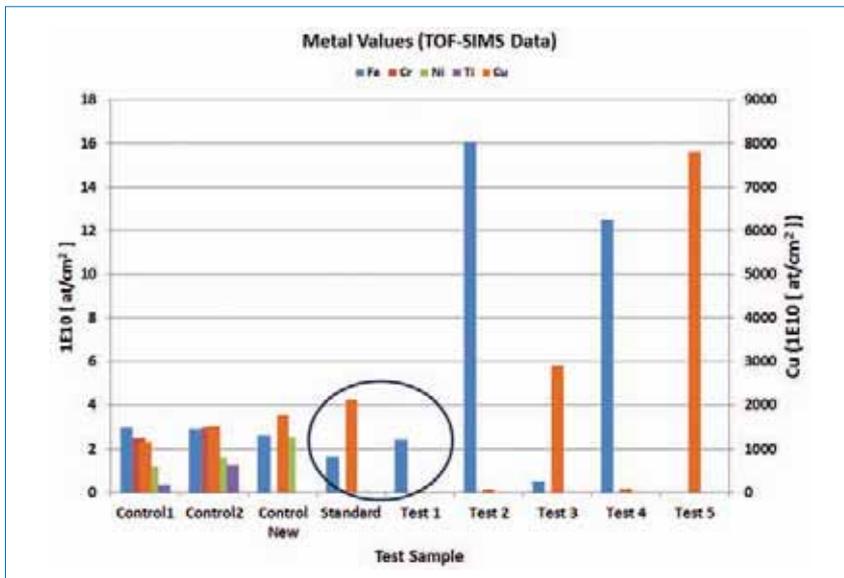


Figure 6. Optimized cleaning sequence (Test 1) vs. Standard Clean; TOF-SIMS results.

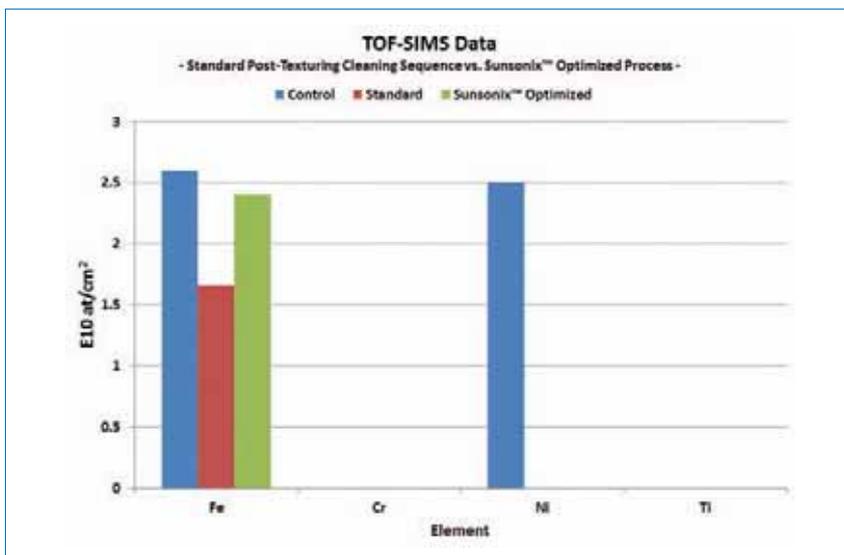


Figure 7. Comparison of standard post-texturing cleaning sequence to best process sequence (Test 1); TOF-SIMS results for Fe, Cr, Ni and Ti.

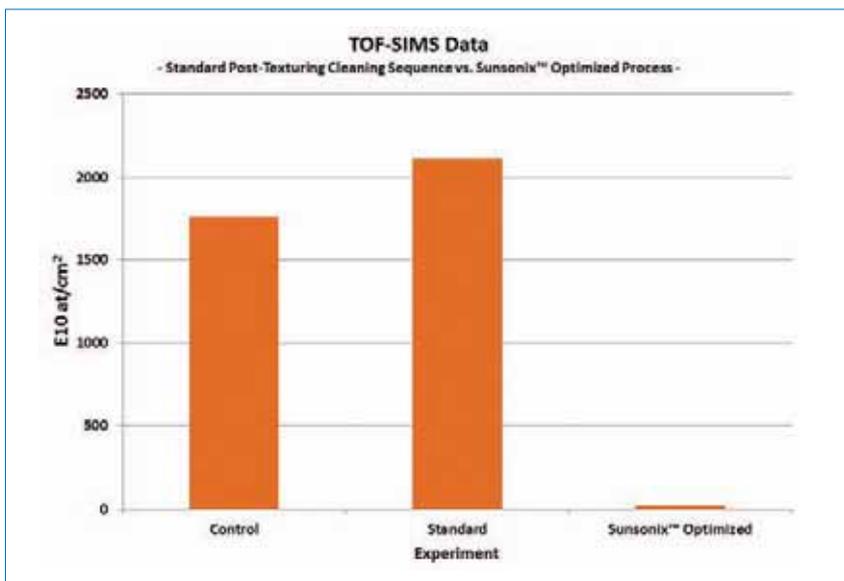


Figure 8. Comparison of standard post-texturing cleaning sequence to best process sequence (Test 1); TOF-SIMS results for Cu.

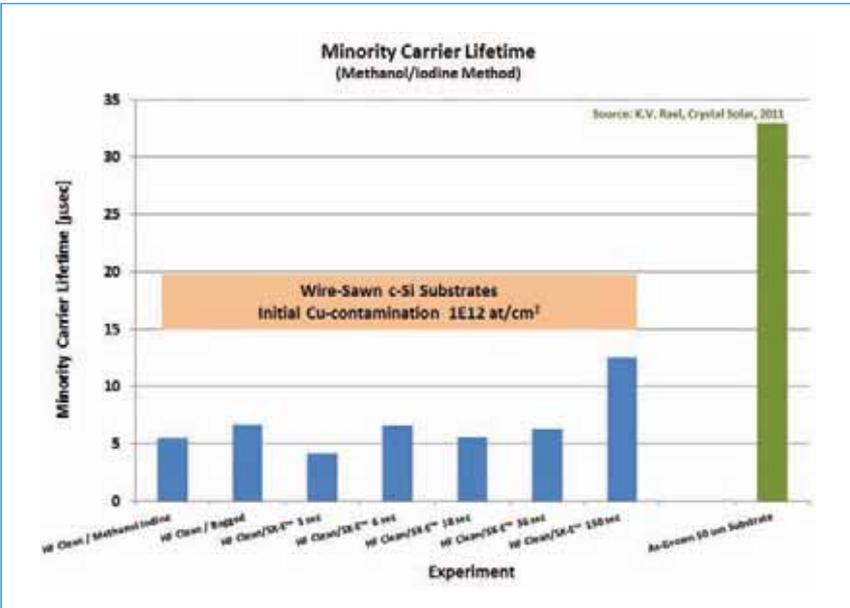


Figure 9. Impact of rinse time on minority carrier lifetime initial decay (see Fig. 14).

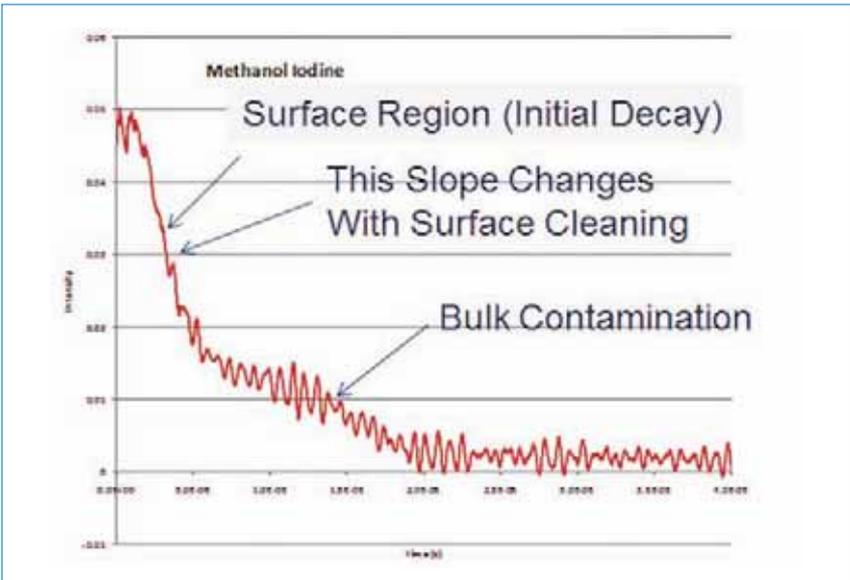


Figure 10. Bi-modal decay indicative of both sub-surface bulk recombination centres.

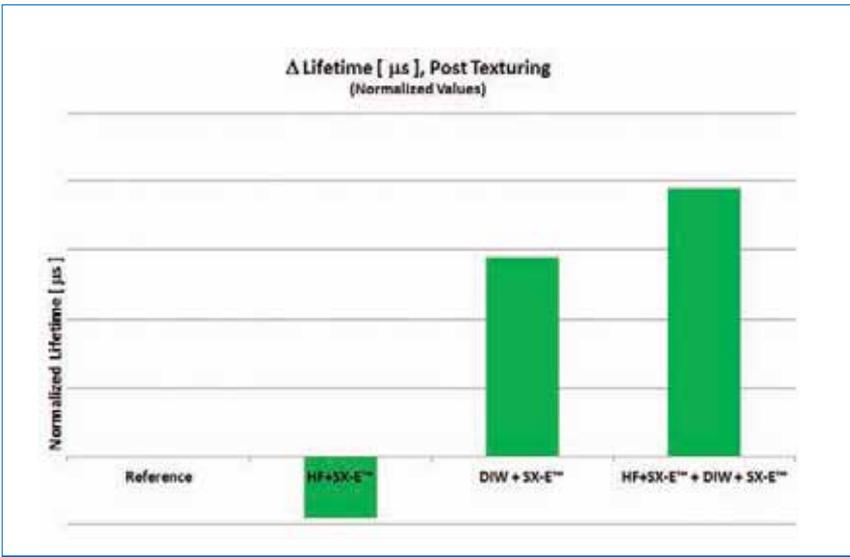


Figure 11a. Customer data; impact of SX-E addition and cleaning sequence on solar cell performance (normalized values post texturing).

in-house process evaluations, using cell manufacturer-supplied production test substrates (mc-Si and c-Si), have provided proof of successful cleaning of trace metals from the surfaces.

The various tests performed narrowed the applicable process sequence for optimum trace metal removal as compared to a standard process sequence (Table 4).

The resulting TOF-SIMS data confirmed that the standard processing shows an overall good removal of trace metals like Fe, Cr, Ni and Ti, but cannot reduce the copper contamination versus the incoming values (Table 4, Fig. 10). Detailed results are depicted in Fig. 7 and Fig. 8.

The careful tailoring of the process sequences, however, removes detrimental trace metal contamination below the detection limits of the analytical methods at hand (TOF-SIMS; see Fig. 8). Of particular note is the Cu level, which is reduced by three orders of magnitude.

“Biodegradable chelating chemistry is effective in controlling trace metals on silicon surfaces.”

High minority carrier lifetime is the key factor when striving for a good operational performance of solar cells. Lifetime influences the open circuit voltage, the short circuit current as well as the fill factor. Lifetime improvement is directly related to the reduction of metallic impurities in silicon, as-received or induced by diffusing metal atoms. It has been determined that effective removal of metal complexes from wafer surfaces is limited by a kinetic step in the aqueous process (Fig. 9). In customer tests, batch processing resulted in cell efficiency gains of 0.2 to 0.3% absolute, compared to no measured improvement for the in-line process. In order to further study this effect, cleaning experiments were conducted on production wafers and the minority carrier lifetime response was measured. As shown in Fig. 9, a doubling of the carrier lifetime was observed at rinse times of 150 seconds or greater. Not surprisingly, the batch process uses a 240-second rinse time, while that of the in-line process uses a bath contact time of 15 seconds.

The measured bimodal decay mechanism observed (Fig. 10) is a direct result of both sub-surface and bulk contamination as shown in Fig. 1b.

**Field tests at cell manufacturer sites**

Using the data obtained through optimization work on a lab scale, best cleaning practices were defined that provided augmented solar cell efficiency.

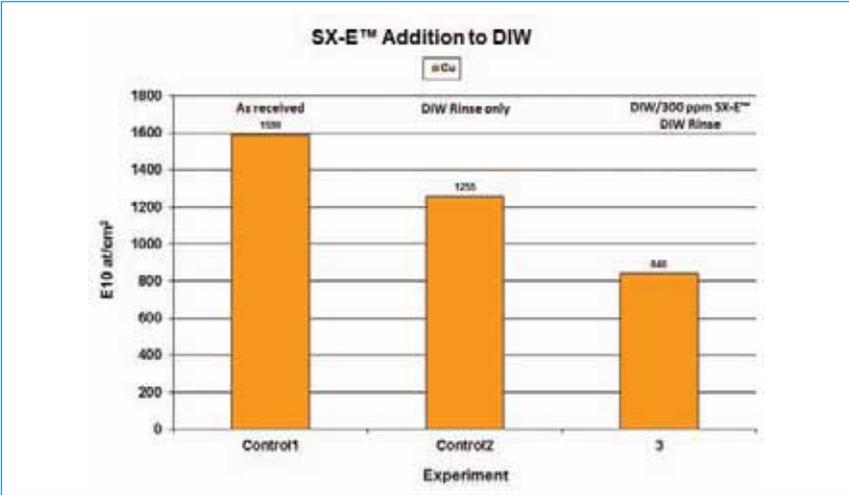


Figure 11b. Addition of SX-E to DIW only reduces the Cu level by about 50%.

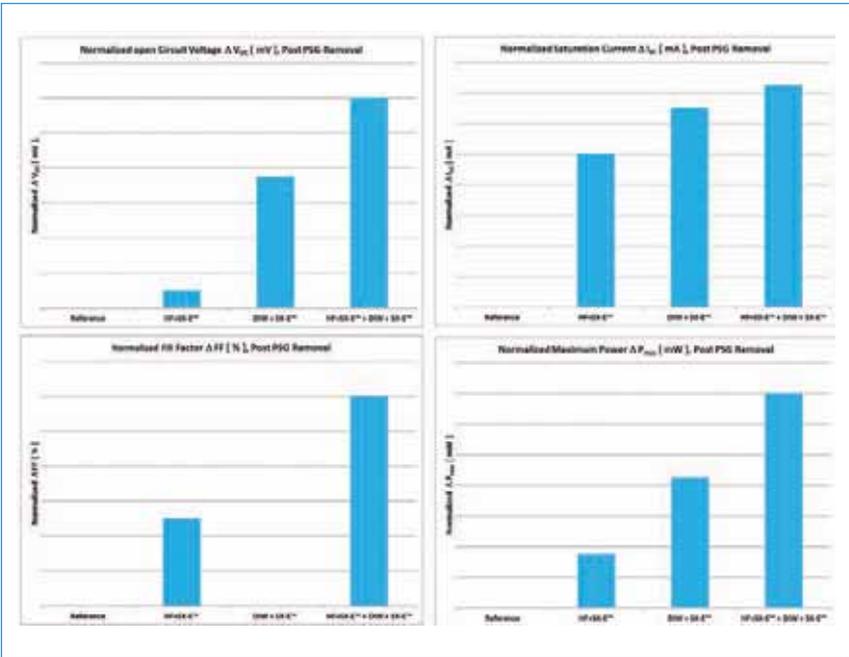


Figure 12. Customer data; impact of SX-E addition and cleaning sequence on solar cell performance (normalized values post PSG-removal).

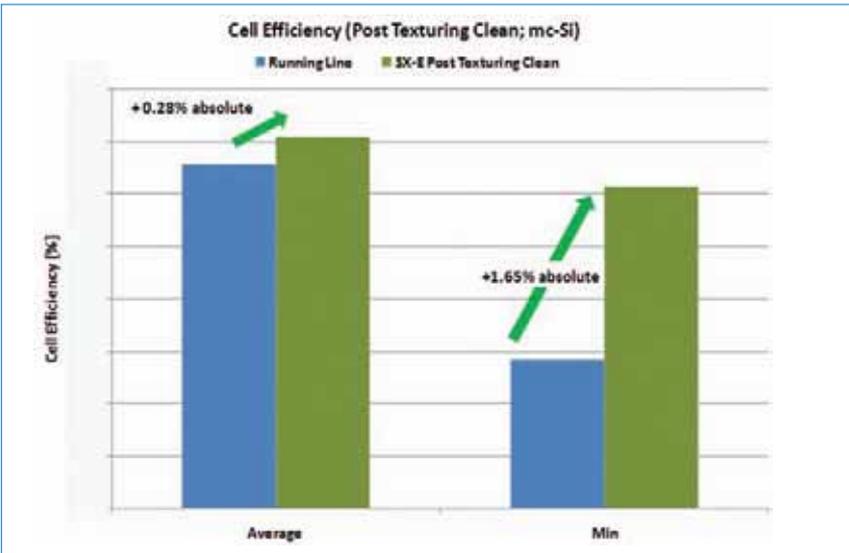


Figure 13. Cell efficiency (post texturing clean; mc-Si); running line vs. SX-E post-texturing clean.

Solar cell manufacturers and substrate manufacturers implemented industrial-scale trials using the best practices developed. These results obtained for both post-texturing clean and post PSG-removal clean correspond to TOF-SIMS data showing:

- Addition of SX-E to HF can be 'hit-and-miss' for effective removal (see also [3], Fig. 11a and Fig. 11b).
- Addition of SX-E to DIW reduces Fe, Ni and Cr levels marginally. The Ti-level is not impacted; copper is reduced by 50% as compared to the as-received level (Fig. 11b).
- Addition of SX-E to both DIW and HF shows an accumulative beneficial effect (Fig. 12a, Fig. 12b).

Metallic impurities close to the Si surface are included into the oxide as the Si surface is chemically oxidized by oxidizing agents, such as dissolved oxygen and H<sub>2</sub>O<sub>2</sub>.

“Narrowing the distribution of cell efficiencies translates to a reduction in mismatch losses when connected into a final PV module.”

Solar cell efficiency distribution in a typical cell line follows a Gaussian type of response. Depending on the sophistication of the manufacturing process, among other parameters, the trail end to lower efficiencies represents a significant financial loss and imposes logistical efforts that can be significantly minimized. Narrowing the distribution of cell efficiencies translates to a reduction in mismatch losses when they are connected into a final PV module. Accounting for mismatch losses ultimately affects the module cost per watt [25]. In earlier manufacturing tests [1], an absolute efficiency increase of 0.2 to 0.3% was reported. In addition, the efficiency spread improved substantially. In fact, the lowest yielding cell efficiencies increased in average by 1.65% (Fig. 13).

**Summary**

Various promising cell concepts from research and development are currently under investigation for commercialization [15]. Standard cleaning processes that have been transferred from the microelectronics industry into PV manufacturing cannot solve the copper contamination issue. Instead of avoiding impurities by 'creative'

or 'intelligent' cleaning, the solar cell industry uses various impurity gettering and removal steps which are marginal and add to the overall operating costs. Effective removal of metal complexes from wafer surfaces has been determined to be limited by a kinetic step in the aqueous rinse process. The first indication of this dependency arises from split lot tests in both batch and in-line processing baths. Trace copper (Cu) impurities are frequently observed from solar-grade Si, which is most likely a result of the wafering process, since standard wires used to slice Si ingots are made of a metallic composite. TOF-SIMS analysis of bare mc-Si and CZ-Si wafers detected  $1.1\text{--}1.8 \times 10^{13}$  atoms/cm<sup>2</sup> of Cu from the samples on the surface. Starting with these contamination levels, further treatment of the metals by use of the complexing agent SX-E, for example, is gaining importance. With the addition of this material to various cleaning process options a reduction of most metallic contaminants from the wafer surfaces is observed. Quantification using TOF-SIMS analysis demonstrates a reduction of copper by *three orders of magnitude* as compared to the as-received level using an optimized process sequence.

In earlier trials, best-of-class cleans have been conducted that increase – in manufacturing split lot trials for both batch and in-line wet cleaning tools – the cell efficiency by 0.3% absolute on multicrystalline Si wafers [1] and on the lowest yielding cells by 1.65% absolute.

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