Cleaning for high-efficiency solar cell processes

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ABSTRACT

This paper discusses the role of wafer cleaning in solar cell processing, and addresses its increasing importance with the introduction of new process steps for manufacturing high-efficiency solar cells. The requirements for cleaning before several process steps, in relationship to the solar cell production sequence, are discussed: front-end-of-the-line (FEOL) cleaning needs to reduce metal surface concentrations by several orders of magnitude (residues from wafer sawing), while back-end-of-the-line (BEOL) cleaning needs to reduce mostly process-induced contamination, which tends to be much lower. A ten-step roadmap for process integration and optimization of new cleaning processes from lab to fab is suggested, which is based on process analytics and simple bath-lifetime simulations. A number of advanced cleaning steps are identified and their suitability for solar cell mass production is examined. The influence of the different input variables is demonstrated, with a focus on feed and bleed settings. Finally, the need for constant monitoring of cleaning baths is highlighted, and a device developed by Metrohm for cost-effective on-site monitoring of metallic contamination is discussed.

Role of wafer cleaning in solar cell processing

'Clean' wafer surfaces in wafer-based silicon solar cell processing are required before high-temperature steps, such as diffusion and thermal oxidation and surface passivation (PECVD, ALD, etc.). The reason for this is that metallic impurities have a detrimental effect on the lifetime of photo-generated carriers. Metallic species act as recombination centres when they penetrate into the bulk, which can happen during high-temperature processes (vulnerability is high notably during thermal oxidation). High diffusivity and solubility in silicon in particular have been reported for iron, copper and nickel [1]. Furthermore, metal impurities can increase the surface recombination velocity [2,3] by increasing the defect density of the interface; they may also lead to leakage currents [4] and may result in junction breakdown [5]. A recent study of the impact of the most common contaminants on solar cell performance when present in silicon solar cells was presented by Coletti et al. [6].

In the following text the importance of efficient and tailored cleaning for high-efficiency processes will be stressed. The main sources of metallic contamination will be addressed, several cleaning-bath mixtures will be discussed and a guide to the successful introduction of new cleaning processes from the process engineering and process analytical side will be given.

> **"Metallic impurities have a detrimental effect on the lifetime of photo-generated carriers."**

The main source of metallic contamination in solar cell manufacturing is the as-cut wafer, which introduces significant amounts of metal impurities that are on its surface. The conventional slurry-based sawing process leaves traces of the sawing wire itself on the surface. As the sawing wire is usually made of a brass- or copper-coated steel wire, the highest measured values of surface contamination are those of copper and iron. Extensive work on the impact of iron and copper contamination on silicon device manufacturing has been carried out [7,8]. However, the contamination level may differ from supplier to supplier (see Table 1), as different wires are available on the market [9,10]. The classical slurry-based sawing process with SiC particles is increasingly being replaced by fixed abrasive diamond-wire sawing [11]. The diamond-wire sawing process is reported to reduce surface contamination [10]; however, copper – a fast-diffusion impurity – is replaced by nickel –another fast-diffusing species – which is found to be especially harmful in near-surface regions [6].

Another source of metal contamination is solar cell process induced. The alkaline etching solution (KOH/NaOH based) – as used for alkaline texturing, saw damage etch or the removal of porous silicon after acidic texturing – cannot be purified the same way as acids; moreover, the high pH value reduces the solubility of metal species and leads to increased wafer surface contamination [9]. The same phenomenon has been observed for non-optimized cleaning solutions that reach critical metallic contamination loads [12].

The metallic impurity sources discussed so far can be considered more or less constant and predictable to a certain extent (as long as the sawing conditions do not differ from batch to batch or the cleaning baths do not encounter critical

Manufacturer	Surface concentration (c_{SF}) [E10 atoms/cm^2]						
	Al	Cr	Cu	Fe	Mn	Ni	Ti
A	600	10	2400	4300	60	210	60
B	2300	30	< 2	680	7	20	210
C	120	10	15600	5200	30	20	100

Table 1. Metallic surface concentration on wafers from different manufacturers [9].

conditions). Defective equipment as the contamination source is less common and more unpredictable, but can have a detrimental effect on the device yield. Although most of the parts in etching machines are made of PP, PVDF or even PFA, there may be unexpected corrosion of wires, screws or other metal parts that are still in use in these machines. This slow deterioration is accelerated by corrosive vapours that are emitted from the etching baths (HCl vapour in particular is known to be extremely corrosive to any metal parts [13, p. 70]).

Contamination from dust in an industrial environment may also occur [1] – a topic that has not been addressed much in solar cell manufacturing, perhaps because it has not yet been perceived as a problem. With cell efficiencies increasing, however, dust contamination may become a problem in the future. While some manufacturers already use advanced and costly clean-room equipment, this is certainly not the standard. In general, unforeseeable and unexpected contamination especially needs to be detected as early as possible in order to prevent yield losses and, potentially, a lengthy and costly search for the source of the problem. So, apart from output-quality monitoring, thorough process monitoring is recommended; how this can be realized will be addressed in the last section of this paper.

Increasing relevance of cleaning for high-efficiency solar cell processes

With the introduction of new process steps, the requirements of wafer cleaning must be re-evaluated. While the phosphorus diffusion process, with its ability to getter metal impurities [14], is relatively robust against surface contamination [15], the same thing may not be said about boron emitter diffusion for n-type junction formation [4,16]. Nevertheless, acceptable gettering efficiencies have recently been demonstrated for boron emitter diffusion [17]. Several process steps – for example, thermal oxidation, passivation with aluminium oxide (Al_2O_3) [18], and deposition of doped amorphous silicon for heterojunction solar cells [19] – are well known for requiring very clean surfaces and also defined surface conditioning. In general, as the efficiency of solar cells increases, through either new process steps or optimization of existing processes, the influence of single steps may become dominant: the losses that have so far been minor will no longer

be covered up by factors such as material quality or poorly optimized steps. A good explanation for this phenomenon is given by Glunz [20], who compares process optimization with fixing a 'leaky bucket', as presented in his keynote speech at the 27th EUPVSEC in Frankfurt in 2012. The optimization and further development of the whole process therefore includes the optimization and/or exchange of cleaning steps.

Large batch / inline processing vs. single wafer handling

Wafer-cleaning technology has a long history in CMOS fabrication [21,22]. To obtain good yields in CMOS fabrication on an ultra-large integration scale, extremely clean surfaces are crucial. Up to several hundred process steps are required for the assembly of microchips, such as CPUs, so that even the smallest amounts of contamination on the wafer surface may lead to device failure and a drastic reduction in yield. Accordingly, process experience has been built up over a long time in this field. At first glance, it seems to be a good idea to draw upon that set of tools and use similar process sequences. However, wafer throughput numbers of the two industries differ by about two orders of magnitude: in solar cell fabrication, up to several thousand wafers per hour are produced, a quantity that large semiconductor factories might not even attain in a week [23]. Consequently, the process specifications are very different.

Highly efficient cleaning sequences, such as the best-known reference procedure, developed by Kern et al. [24] at the *Radio Corporation of America* (and hence called the RCA cleaning sequence), might be suitable for research and development applications but not for mass production of solar cells. The number of steps of the standard clean 1 (SC-1) and standard clean 2 (SC-2) is high, and these steps require high temperatures and long process times, which massively influence cost of ownership.

Another cleaning sequence that is in use in research labs (which is the process of record – POR – at ISC Konstanz), and also borrowed from IC manufacturing, is SPM (sulphuric-acid hydrogen-peroxide mixture) based [25]. However, this sequence cannot be introduced into solar cell mass processing, because the highly corrosive solution enriches water as it oxidizes the surface of the wafers, and hence dilutes itself, so as a result the bath has to be frequently replaced [13, p. 73].

Even in semiconductor manufacturing, the need for simplification has been recognized, and some approaches – the introduction of ozone-based cleaning solutions, for example – have also been published [26]. Some of these alternatives are discussed below. It should be stressed here that, if CMOS processes are to be mimicked for solar cell mass production, thorough testing as regards their suitability and cost effectiveness is required.

From lab to fab

In order to implement new process steps in existing solar cell production lines that are assumed to require advanced cleaning, the following ten-step scheme is suggested.

1. Choose a suitable test structure.

2. Test whether pre-existing industrial cleaning can replace the laboratory cleaning sequence.

3. Evaluate the optimization potential of the industrial process.

4. Choose a 'new', advanced cleaning procedure.

5. Collect input variables for the mass production simulation (by process analytics).

6. Simulate bath ageing.

7. Artificially age the bath, and test the cleaning efficiency.

8. If not suitable, try optimization.

9. Integrate the new process step into the process sequence.

10. Monitor the bath and surface concentrations.

To optimize costly pilot-line testing, the authors suggest working with a simple (e.g. Excel based) cleaning-bath simulation tool, and processing analytical methods in combination with artificial bath ageing to obtain information about mass production suitability.

Since the processing of complete solar cells (at least on a lab scale) is time and resource consuming, it is usual for simplified test structures to be used to obtain the relevant information (**1**). Common test structures for process optimization are symmetrical minority-carrier lifetime samples, which can be used for qualitative and quantitative

comparisons of the influence of different process conditions on electrical solar cell properties. In order to gain a more complete picture, cell precursor structures can be fabricated (performed as shown in Fig. 1) and measured by QSS-PC. The implied V_{oc} values obtained in this way yield valuable information about losses due to recombination that is induced by metallic impurities. The advantage of this kind of structure is that metallization losses, often the dominant losses in cell voltage due to metallization–silicon interface recombination [27], are left out of the picture, and the smaller factors, such as cleanliness, become more evident.

Figure 1. Implied V_{oc} of BiSoN precursor structures (solar cells without metallization), as measured by QSS-PC.

Is advanced cleaning really necessary?

An example of the need for new, advanced cleaning procedures is given in Fig. 1; for this, N-type BiSoN solar cell precursors were manufactured. ISC Konstanz's baseline process for bifacial n-type solar cells using only standard industrial process equipment and screen-printing metallization achieves up to 20% energy conversion efficiency, as reported by Edler et al. [27] at this year's EU PVSEC in Paris. In this experiment the current POR for pre-diffusion cleaning – a time- and chemical-consuming lab-only cleaning sequence for both the boron and phosphorus diffusion – was replaced by a standard industrial HCl+HF cleaning sequence (**2**): in consequence, a loss in implied V_{oc} of almost 10mV was recorded.

Sometimes, however, existing cleaning procedures may be optimized without the need to replace them (**3**). It has been suggested that the cleaning efficiency of an HCl step increases with lower HCl concentration [28]; in turn, the dosing volume can be increased in order to reduce bath contamination load, and moreover the net chemical consumption can be reduced. This approach, however, is unlikely to work with surfaces that are highly contaminated (especially by copper), such as after initial saw damage removal or alkaline texturing. Furthermore, potential organic residues will not be removed. An alternative, which might also help, is the addition of complexing agents: one example is SX-E, which will increase the solubility of metallic species, as reported by Treichel et al. [29].

Available cleaning-bath solutions and procedures for advanced cleaning
When the optimization of existing cleaning baths is not possible, a new,
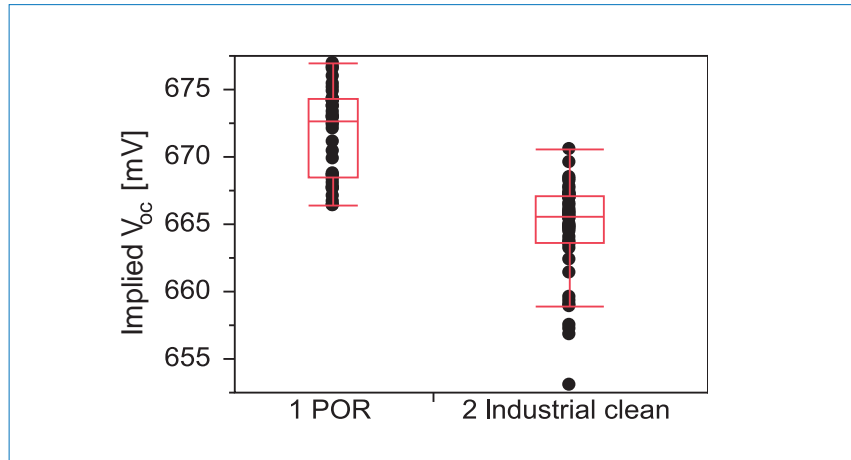
more advanced cleaning sequence needs to be chosen (**4**). Good cleaning efficiencies are ensured when cleaning solutions with a high oxidizing potential are used (possible examples are listed below). Oxidizing solutions can prevent the outplating of noble metal species (most notably copper) on the silicon surface. Furthermore, they can remove the organic contamination that remains on the surface as a result of wafer sawing or from texturing additives used for cleaning the incoming wafers or for post-texturing cleaning. In most cases a final HF dip is used to remove the sacrificial oxide layer from the surface in order to render the surface hydrophobic. It might be worth considering the use of a mixture of diluted HF and diluted HCl here, to prevent copper plating (copper has a low solubility in HF and a strong tendency for outplating [19]). Between the cleaning bath and the oxide removal step, wafers need to be rinsed in deionized water, to reduce water consumption – usually rinsing cascades are used for this. If a hydrophilic surface is required, ozonated water may be used as the last cleaning step.

> **"Good cleaning efficiencies are ensured when cleaning solutions with a high oxidizing potential are used."**

When oxidizing cleaning solutions are used to clean highly doped regions, etching of the surface can occur and a change in sheet resistance may be observed, which has to be taken into consideration. Moldovan et al. [30] showed that this effect can be used to advantage for a controlled emitter etch-back in ozone-based cleaning solutions. The following (incomplete)

list is a collection of advanced cleaning solutions that have been suggested or designed for use in solar cell processing.

- SC-1 (only)
- SC-2 (only)
- H_2O/O_3
- HF/O_3
- HCl/O_3 or combination of HCl and HF
- SELURIS clean
- SX-E

The listed cleaning solutions are divided into three groups. The first group is simply the split-up RCA process sequence. Typically, SC-1 consists of ammonia (NH_3OH) and hydrogen peroxide (H_2O_2); it has excellent particle removal performance and will also remove organic contamination. SC1, however, is less effective in removing metallic impurities (especially at higher bath contamination loads, since H_2O_2 decomposition is catalyzed by metallic species). A less costly alternative is a mixture of NaOH with H_2O_2, often referred to as pseudo SC-1 (pSC-1); the major disadvantage of this is the need for thorough H_2O_2 control, as too low a concentration will increase the etch rate significantly, so that polishing of the surface may occur.

The SC-2 cleaning solution is a mixture of HCl and H_2O_2, and reportedly has a very good cleaning efficiency for metallic impurities [13]; however, the H_2O_2 decomposition at low pH-values is catalyzed by Cl$^-$ ions. A lengthy discussion and summary of SC-1 and SC-2 can be found in Reinhardt et al. [13]. In general, (p)SC-1 and SC-2 require high temperatures for best performance: 70–80°C is suggested. The H_2O_2 consumption at these temperatures is high, so – in the authors' opinion – neither of these cleaning solutions is suitable for transfer to solar cell mass production.

The second group – ozone-based cleaning solutions – seems to be more promising. The oxidizing species O_3 is usually dissolved with a contacting membrane and has a relatively short half-lifetime in solution, which simplifies disposal. Once purchased, ozone-generating equipment operates at a relatively small running cost [31,32]. Ozone-based cleaning solutions usually work with low acid concentrations (or even with no added acid) [30,33], so chemical consumption for feed and bleed processing is low. Heating is not required, and higher ozone solubility is achieved using lower temperatures [34].

The last group comprises two commercially available additives, both based on biologically degradable complexing agents. SELURIS C by BASF is the main component of an alkaline cleaning mixture with H_2O_2 and water. With this recipe, low H_2O_2 decomposition and (hence) low H_2O_2 consumption have been claimed [35,36]. The SX-E approach by Sunsonix is not really a stand-alone solution but an additive that can be mixed with any existing cleaning solution, boosting its efficiency [29,37].

A critical factor related to the introduction of new processes, especially with new machines, is the ability to monitor the reagent concentration, most importantly when one or more components are consumed during the process, as in the case of H_2O_2. Monitoring can be a simple operation, especially with a small number of ingredients (e.g. monitoring by titration), but can be complex when there are multiple ingredients involved. Nevertheless, monitoring reagent concentrations is crucial for cost-effective processing, as a waste of expensive chemicals, or the loss of cleaning efficiency through a slowly changing bath make-up, can be avoided.

> **"Monitoring reagent concentrations is crucial for cost-effective processing."**

Simulation of cleaning-bath lifetime
To determine the connection of throughput and initial contamination level with cleaning-bath performance (**5+6**), a simple Excel-based simulation tool can be used: in combination with analytical methods, this enables one to obtain detailed information about process requirements, process stability and cleaning mechanisms. The variables used in this simulation are summarized in Fig. 2.

Surface contamination needs to be measured before and after cleaning. In this study the data for surface contamination was collected using the sandwich-etch extraction method to dissolve surface and near-surface metallic species, as described by Buchholz et al. [9], and measurements were then carried out by ICP-MS. The advantage of this method is that sampling can be performed on site to avoid risk of contamination during transportation; moreover, virtually all kinds of wafer surface in silicon solar cell processing can be measured. Using these measurements, the first simulations can be run by inputting bath size, throughput, and feed and bleed settings. The bath volume is usually kept constant independently of the dosage and carry-over from the previous bath by an overflow. The more information that is available, the more accurately the simulation will work. Variables that can be added are, for example, background contamination levels (of a new cleaning bath), certificates of analysis of the
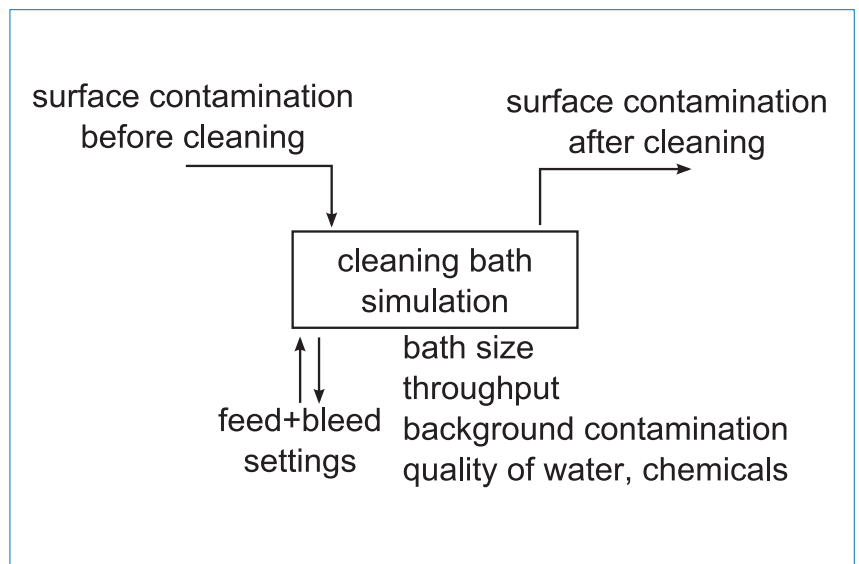

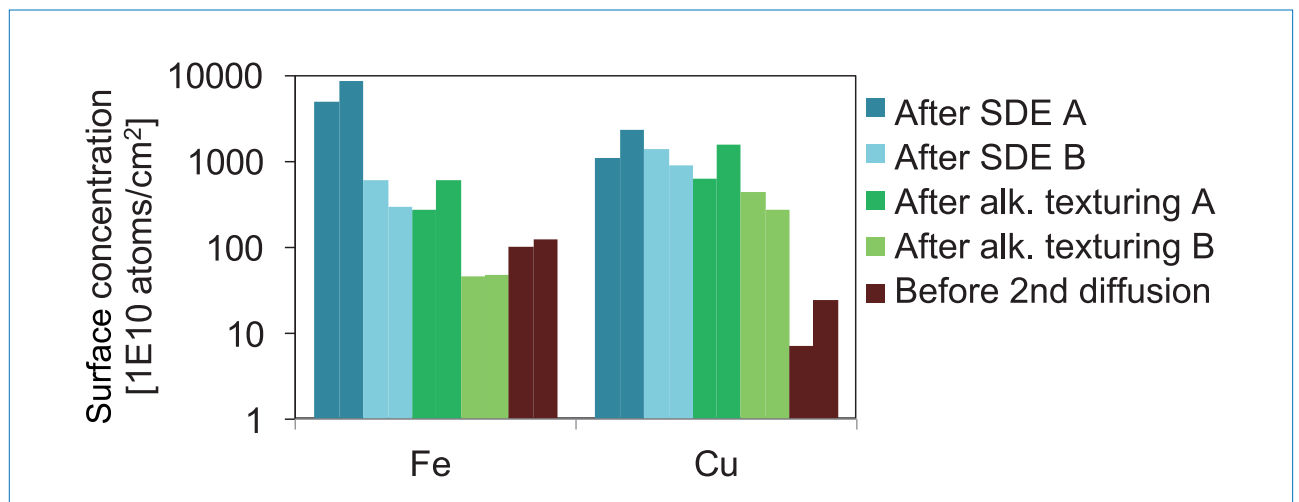**Figure 2. Schematic of the cleaning-bath simulation tool.**

Figure 3. Iron and copper surface concentrations after saw damage etch and alkaline texturing (FEOL) on two different days, as well as before the second diffusion (BEOL), in the aforementioned BiSoN process (two measurements for each sampling point).

as-delivered chemicals, water purity levels, and carry-over from the previous bath (usually rinsing water).

Fig. 3 illustrates the significant variations in surface contamination of iron and copper at different steps in the process chain: cleaning at different stages of the process (front end of the line, FEOL, vs. back end of the line, BEOL) therefore needs to be assessed differently.

The impact of different initial surface concentrations on the bath contamination load, according to the simulation in this study, can be observed in Fig. 4; similar clean surfaces after cleaning, independently of the initial level, and the same process set-up (200L cleaning bath, 1mL/wafer is replenished), are assumed. Under constant feed and bleed conditions, with a constant intake of metal surface contamination, the contamination load of a cleaning bath will eventually reach equilibrium. It is evident from Fig. 4 that different conditions, such as a variation in initial contamination, can significantly alter the etch bath conditions. What has not been taken into account here is that the cleaning efficiency may be reduced by the enrichment of the specific species in the bath: critical concentrations need to be determined experimentally.

Experimental determination of critical concentrations / artificial bath ageing

Before the introduction of a new cleaning sequence into the process sequence, the cleaning bath can be artificially aged (**7+8**) in order to avoid actual large-scale production. Different feed and bleed scenarios should be tested (see Fig. 6), so that the most cost-effective scenario (with sufficiently high cleaning power) can be chosen. Cleaning-bath ageing is most easily realized by spiking lab-scale cleaning baths, for example by using atomic absorption spectrometry (AAS) single-element standard solutions. An example of the combination of cleaning-bath simulation and testing for process suitability in the case of two different cleaning solutions (HF/O_3 and SELURIS) is given in Fig. 5, as presented by Buchholz et al. [12] at this year's EU PVSEC.

The first graph (top left Fig. 5) shows the enrichment according to an enrichment simulation with similar parameters to those used in the simulation in Fig. 4: 500E10 atoms/cm^2 of copper (red curve) and 1000E10 atoms/cm^2 of copper (blue curve) were used as initial contamination levels. The second graph (top centre Fig. 5) shows

the cleaning efficiency of a spiked cleaning bath (0ppb, 5ppb, 305ppb): a reduced copper removal efficiency was found for the HF/O_3 bath spiked with 305ppb of copper, while in the case of SELURIS there was no sign of cleaning efficiency reduction. To check whether critical concentrations had been reached, symmetrical lifetime samples were processed using the following process sequence. The as-cut wafers were textured using KOH/RENA monoTEX. The wafers were then cleaned using different cleaning procedures, and different copper contamination levels were obtained by spiking these cleaning solutions. Next, the wafers were diffused using BBr_3 in a tube diffusion furnace, and both sides were passivated using a silicon oxide-nitride passivation stack.

The implied V_{oc} values with different copper contamination levels are plotted in the third graph (top right Fig. 5). Only a small loss in implied V_{oc} is expected from the reduced cleaning efficiency. However, the first two data points already show a statistically significant decrease in implied V_{oc} for symmetrical minority-carrier lifetime samples of ~2mV. To be on the safe side (especially when expecting higher initial surface

contamination), an increase in feed and bleed volume would be advisable for the HF/O$_3$ process step, resulting in curves similar to those in Fig. 6: an increase from 1mL per wafer to 5mL per wafer reduces the cleaning-bath load considerably. If such modifications are to be implemented, the cost of additional chemical consumption and disposal of used cleaning solution needs to be taken into account. With very low HF concentrations, it might actually be a feasible option for improving the cleaning performance of such a cleaning-bath solution.

Monitoring of cleaning-bath quality

The importance of monitoring impurity concentrations was stressed earlier. On the one hand, cleaning baths can be optimized and controlled to ensure cost-effective processing (**10**); on the other hand, unexpected failures, such as defective equipment, can be detected at an early stage. Analytical technology, however, is often very costly, and/or it may take several days for the results to come back, as samples need to be sent to an analytical laboratory. ICP-MS analysis of wafer surfaces may easily cost up to several hundred or even thousand Euros. Nevertheless, for process analytics and process optimization, this technique cannot very easily be replaced, as it provides a quantitative analysis of many elements simultaneously, with a very low limit of detection. When such samples are required, such as for the above-described introduction of new cleaning processes, a thorough planning of experiments is strongly advised.

Analytical technology, however, is not really suitable for the constant monitoring of cleaning and/or rinsing baths. It is for this reason that Deutsche Metrohm Prozessanalytik and ISC Konstanz have developed and tested a photospectroscopic method which uses the colour of metal complexes to determine the level of contamination by iron and copper, the two most common metallic impurities; it has so far been tested and optimized for diluted HF, HCl (0.05–3%) and water. The complete method is incorporated into a fully automated Metrohm ProcessLAB. The entire sample preparation procedure is managed by a liquid-handling module that is controlled by tiamo (the Metrohm software for titration, control of the modules and data handling), in which the data is also processed and stored. Before and after each analysis stage, the entire system cleans itself automatically. The calibration of the system is performed by adding specific amounts of an iron/copper mixture to a blank solution. The method developed can be used to constantly monitor the quality of the process and of the cleaning baths: early detection of harmful enrichment or contamination from defective equipment is therefore possible. The system also allows the monitoring of most of the baths in use before the critical (i.e. high-temperature or passivation) steps, and may be used as a platform for the development of techniques for additional elements and cleaning baths [38].

" Fundamental knowledge about cleaning-bath performance and the input variables is crucial for efficient and cost-effective cleaning in solar cell mass production. **"**
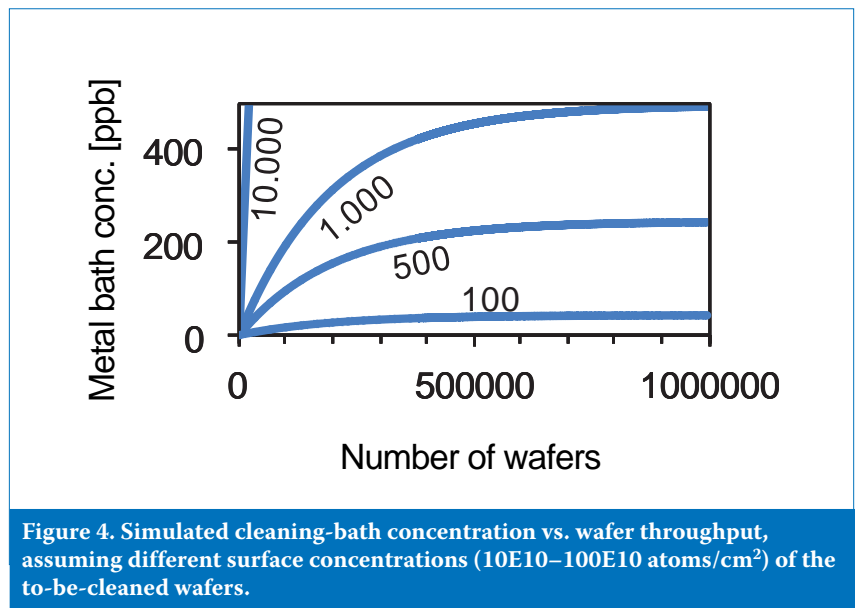

Figure 4. Simulated cleaning-bath concentration vs. wafer throughput, assuming different surface concentrations (10E10–100E10 atoms/cm^2) of the to-be-cleaned wafers.
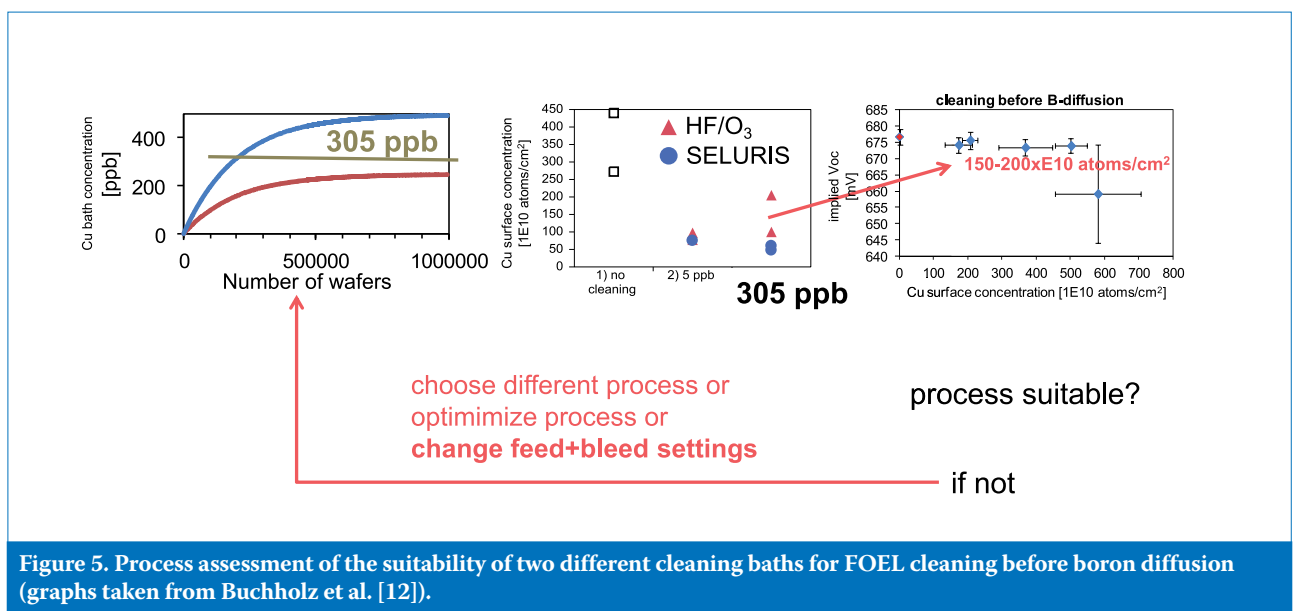

Figure 5. Process assessment of the suitability of two different cleaning baths for FOEL cleaning before boron diffusion (graphs taken from Buchholz et al. [12]).
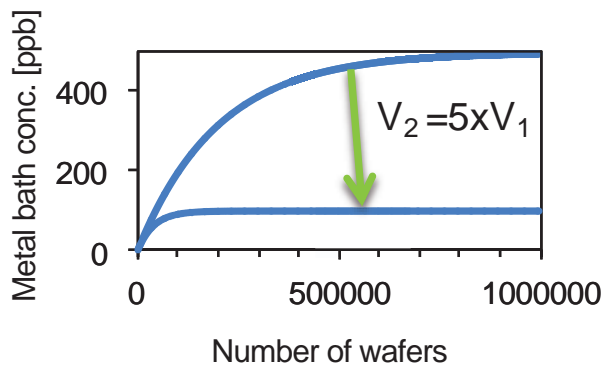
$$V_2 = 5 \times V_1$$

Figure 6. Simulated cleaning-bath concentration vs. wafer throughput: feed and bleed volume at high throughputs is five times as high.

Conclusion

The relevance of wafer-cleaning technology for high-efficiency solar cell processes has been summarized in this paper. O_3-based cleaning appears to be promising; there are, however, other highly efficient cleaning solutions available. Fundamental knowledge about cleaning-bath performance and the input variables, such as metallic surface contamination, is crucial for efficient and cost-effective cleaning in solar cell mass production. A ten-step scheme for the introduction of new process steps into existing lines and/or new solar cell lines has been proposed, with a focus on feed and bleed parameters. FEOL cleaning in particular is highly demanding, as the contamination from the wafer surface can vary from batch to batch. In-line analytical facilities are recommended in order to assure the quality and maintain high yields, especially when unexpected contamination occurs.

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