

2AV.5.14: Pre-Diffusion Clean Optimization for High-Volume Manufacturing of Multi-Crystalline Solar Cells

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ABSTRACT: The cost of chemical waste disposal is high. It is therefore important for the PV industry to find ways to reduce chemical consumption and waste generation through chemical usage reduction, recovery, recycle, reuse, and substitution. Iron, cobalt, nickel, titanium and copper are important metals that when present on a silicon wafer surface adversely influence the efficiency of resulting PV devices. However, many of these surface ions can be effectively removed during wafer cleaning by the addition of a complexing or chelating agent (such as SX-E™). In this paper, we explore the process optimization as well as the removal of several of these metal ion complexes.

Keywords: mc-Si, Production, Optimization, Characterization, Experimental Methods, Fundamentals, Photovoltaic, Wet Cleaning

1. INTRODUCTION

According to the economy of scale the productivity of tools needs to improve by increasing yield and cell efficiency, throughput of a production line as well as the reduction of labor cost and tool and consumable cost per product. With respect to the first factor, transition metal contamination is thought to be one of the major factors contributing to photovoltaic carrier lifetime degradation and thus efficiency. Metals can be introduced into mc-Si wafers from the feedstock silicon. 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 solution [1, 2]. While gettering can reduce the amount of metal contaminants in the cells, additional contaminants can also be introduced during processing due to the relatively lenient requirements for the cleanliness of the production environment at a typical photovoltaic facility. The addition of a chelator to enhance the removal of metallic ions has been effectively used to reduce surface contamination of RCA-derived cleaning chemistries [3]. These chelator molecules typically feature conjugated double bonds.

The cost of chemical waste disposal is also high. It is therefore important for the PV industry to find

ways to reduce chemical consumption and waste generation through chemical usage reduction, recovery, recycle, reuse, and substitution. The silicon PV industry uses significantly less water per wafer than the IC industry. However, the value of the final product per wafer of the PV industry is orders of magnitude less than that of the IC industry. Obviously, water use by the PV industry is a significant cost factor that needs to be minimized.

2. EXPERIMENTAL

While batch-type working wet benches are the first choice for cleaning and alkaline texturing of monocrystalline wafers, the manufacturing lines of multicrystalline solar cells preferably apply acidic texture processes on inline-working machines. Though in-line tools are the current toolset of choice for high volume manufacturing of mc-Si PV cells, the tool setup and process sequence leaves room for significant improvement. A typical pre-diffusion cleaning sequence is shown in figure 1.

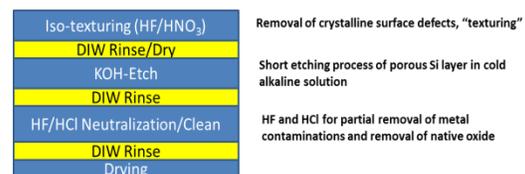


Fig. 1: Typical mc-Si in line pre-diffusion cleaning sequence

Due to the nature of the tool build and the installed process, there are obvious limitations:

- DIW rinse is too short and can only be performed in cold water at exorbitantly high overflow values (> 900 liters/hour)
- Etchant and neutralization steps are un-optimized, in particular the chemical concentrations used
- Application of a complexant is compromised due to the overflow conditions and the limitations of the DIW rinses with respect to reaction kinetics.

In order to improve the process results, the following experiments were carried out:

1. Addition of SX-E as a complexant to various process steps
2. Decrease overflow to minimum for the so-called Rinse-2 in between the KOH and HF step
3. Variation of the HF/HCl ratio
4. Combinations of various process conditions

To ensure statistical significance, a minimum of 100 substrates for the screening and typically 1000 substrates for the fine-tuning were processed.

3. BASICS [4]

3.1. Series Resistance

As the series resistance increases, the voltage drop between the junction voltage and the terminal voltage becomes greater for the same current. The result is that the current-controlled portion of the I-V curve begins to sag toward the origin, producing a decrease in the terminal voltage V and a slight reduction in I_{SC} , the short-circuit current. Higher values of R_S will also produce a reduction in I_{SC} ; in these regimes, series resistance dominates and the behavior of the solar cell resembles that of a resistor.

3.2. Shunt Resistance

As shunt resistance decreases, the current diverted through the shunt resistor increases for a given level of junction voltage. The result is that the voltage-controlled portion of the I-V curve begins to sag toward the origin, producing a decrease in the terminal current I and a slight reduction in V_{OC} . Low values of R_{SH} will produce a reduction in V_{OC} . As in the case of a high series resistance, a badly shunted solar cell will take on operating characteristics similar to those of a resistor.

3.3. Short Circuit Current

The short-circuit current is due to the generation and collection of light-generated carriers. For an ideal solar cell at most moderate resistive loss mechanisms, the short-circuit current and the light-generated current are identical. Therefore, the short-circuit current is the largest current which may be drawn from the solar cell and depends strongly on the generation rate and the diffusion length.

3.4. Open Circuit Voltage

Open-circuit voltage is a measure of the amount of recombination in the device. Where the short-circuit current (I_{SC}) decreases with increasing bandgap, the open-circuit voltage V_{OC} increases as the band gap increases.

3.5. Fill Factor

FF is a measure of the "squareness" of the IV curve. The "fill factor", more commonly known by its abbreviation "FF", is a parameter which, in conjunction with V_{OC} and I_{SC} , determines the maximum power from a solar cell. The FF is defined as the ratio of the maximum power from the solar cell to the product of V_{OC} and I_{SC} .

4. RESULTS AND DISCUSSION [4]

Experiment	Change	SX-E Addition	Efficiency	FF	V _{OC}	R _{SH}	R _S	J _{SC}	Comment
STD	Std., 900 lph overflow in Rinse 2								Baseline Values
Std., Reduced DIW	Rinse 2 Overflow decreased to 300 lph	N	↔	↔	↔	↑	↓	↔	
KOH+SX-E	Rinse 2 Overflow decreased to 300 lph	300 ppm	↓	↑	↓			↓	
Rinse2+SX-E	Rinse 2 Overflow decreased to 300 lph	150 ppm	↓	↓	↔	↑	↑	↓	
Rinse2+SX-E	Rinse 2 Overflow decreased to 300 lph	300 ppm	↑	↑	↔	↑	↑	↓	
Rinse2+SX-E	Rinse 2 Overflow decreased to 300 lph	450 ppm	↓	↓	↔	↓	↑	↔	
STD	HF (4%)/HCl (8.4%)								Baseline Values
HF (4%)/HCl (8.4%)+SX-E	Adding SX-E to HF/HCl	300 ppm	↔	↔	↔	↓	↓	↔	
HF(4%)/no HCl + SX-E	Reduce HCl to 0%	300 ppm	↓	↓	↓	↓	↑	↔	
HF(4%)/HCl (0.04%)+SX-E	Reduce HCl to 0.04%	300 ppm	↓	↑	↔			↓	
HF(4%)/HCl (0.02%)+SX-E	Reduce HCl to 0.02%	300 ppm	↔	↔	↔	↑	↔	↔	
HF(2%)/HCl (0.02%)+SX-E	Reduce HCl to 0.02% and HF to 2%	300 ppm	↓	↓	↔			↓	
STD	Std., 900 lph overflow in Rinse 2								Baseline Values
HF(4%)/HCl (0.02%)	Reduce HCl to 0.02%	N	↔	↔	↔	↘	↔	↔	
	↑	Upwards Trend							
	↔	No significant Change							
	↓	Downwards Trend							

4.1. Addition of SX-E to KOH:

SX-E gets trapped in the porous Si generated by the acidic texturing step and prevents complete removal of trace metals because of competing surface desorption kinetics during a fast rinse cycle.

4.2. Addition of 300 ppm SX-E to Rinse 2:

V_{OC} stays the same or increases modestly, J_{SC} decreases but FF goes up (giving better efficiency). This is because metals are not diffusing back into the bulk of the wafer during the emitter formation. When both J_{SC} and FF go up one can get 0.15 to 0.25% absolute efficacy increases. Excess of SX-E worsens the results.

4.3. Reduction of DIW Overflow in Rinse 2:

Decreasing the DIW overflow from 900 liters/hour to 300 liters/hour results in:

- Equal or better cell parameter
- **Saving of 6 million liters of DIW** (generation and disposal) per 100 MW production, per year

It costs approximately \$12 to generate 1000 gallons of DI water. Therefore the monetary saving for the DIW generation alone equals about \$20,000 per year per 100 MW productions.

4.4. Addition of SX-E to HF/HCl; Variation of HF to HCl ratio:

- FF goes up with decreasing HCl concentration and increasing HF concentration
- J_{SC} goes up with both HCl and HF concentration
- At low HCl concentrations, low DIW overflow condition and SX-E addition electrical parameters compared to baseline are pretty much the same, except the R_{SH} goes up

4.5. Reduction of HCl concentration:

Decreasing the HCl concentration from 8.4% to 0.02% results in:

- Equal or better cell parameter
- **Saving of 4200 liters of concentrated HCl** per 100 MW production, per year

This equals a monetary saving of \$21,000 per year per 100 MW production with an assumed price of \$ 5 per liter concentrated HCl.

The problem with in-line tools is the short immersion times in the chemical modules and DIW rinse modules. The fundamental issue regarding the in-line tools is that the reaction of the SX-E molecule with the metal ions at the surface of the wafer takes time. This kinetic limitation of the chemistry can be overcome by increasing the temperature of the chemical module and DIW rinse module. The activation energy of the SX-E reaction is such that the rate doubles for every 10 °C increase in temperature. The baths on the inline tools do not

have provisions for heating and the current operating temperature of these baths is around 25-30 °C. Obviously, since these temperatures are not controlled, then process repeatability might be difficult when applying “copy exact” to different photovoltaic fabs. We suggest increasing the bath temperatures to 80° C, which would result in an increase of reaction rate by a factor of 32. We believe this will be sufficient to realize the results achieved in the batch tools (30 °C temperature). The residence time in those tools for validation tests was about 90 seconds. Unfortunately the immersion times in the in-line tool for both chemical modules and DIW rinse modules is between 10 and 15 seconds. Therefore by increasing the temperature to 80 °C the effective normalized immersion time increases to 450 seconds, certainly enough time to achieve the desired metal removal with SX-E chemistry.

5. SUMMARY AND CONCLUSIONS

Our studies have shown that control and optimization of the cleaning process, enabling benefits such as substantial savings with regards to water and chemical usage in volume production can be achieved. The fundamental issue regarding the in-line tools is that the reaction of the SX-E molecule with the metal ions at the surface of the wafer takes time. This kinetic limitation of the chemistry can be overcome by increasing the temperature of the chemical module and DIW rinse module to e.g. 80°C.

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