Solar Cell Texturing: A Simplified Recipe

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This paper presents a method for cost reduction and green processing of silicon-based solar cells by replacing post-texturing cleaning baths with simplified rinsing processes. Reduction of the amount of chemical and water used is demonstrated. The rinsing processes can be used for post-acidic texturing with HF/HNO_3 or alkaline-based texturing with KOH. Rinses with low-concentration of chemicals have been show to be just as effective as concentrated chemicals. Results show that the initial texturing topology and reflectivity is not affected by the subsequent rinses and the doping uniformity is also the same as with the standard chemicals.

Background

Texturing of the surface is the first step of the single emitter photovoltaic (PV) manufacturing process for both mono- and multi-crystalline silicon wafers. In addition to texturing, the initial wet chemical process also removes saw-damage, undesirable contamination, and then renders a hydrophobic silicon surface to allow uniform doping for the emitter formation. The texturing process roughens the surface and reduces the reflection of the silicon surface by etching along crystal planes and grain boundaries to increase the surface area to provide more light trapping.

Both wet chemical and plasma processing yield the necessary saw-damage removal, texturing, and pre-doping surface conditioning for mono-crystalline or multi-crystalline (1) cells and are cost effective. Wet chemical processing is used for high volume PV production because of the low manufacturing cost, which allows solar cells to be competitive with non-renewable energy sources. Cost reduction measures are in great demand in the PV industry to allow grid parity to be reached. Therefore, the focus of this paper is to introduce cost reduction; by simplifying the post-texturing cleaning and rinsing baths used for the wet texturing process for multi-crystalline silicon.

The ECN (Energy Center of The Netherlands) process is a commonly used wet texturing process for multi-crystalline Si. The optimized T2 process uses a two-step texturing bath to achieve the optimum efficiency of approximately 17% for single emitter photodiodes (2). The ECN T1 (3) or the Universitat of Konstanz process, also known as the UKN (4) texturing process, and other low-etch rate texturing processes for thin wafers (5) can also be used. All these processes utilize a HF/HNO_3 acid texturing bath that also removes the saw damage. Additionally, KOH with IPA or a surfactant (6) or NaOH, can also be used as the texturing bath, alone or sequential after the HF/HNO_3 acid bath for multi-crystalline silicon. For mono-crystalline Si, the preferred texturing solution is alkaline-based. If an acid texturing bath is used, a KOH or NaOH bath is used after it to remove the porous that silicon remains on the surface. An HF/HCl bath is typically performed after the alkaline hydroxide step to facilitate removal of the mobile

ions, metallic contamination, and to strip the chemical oxide. The final oxidation step creates a homogeneous hydrophilic surface allowing uniform phosphorus doping to create the emitter (7). Figure 1(a) shows a common flow for each chemical bath and rinsing step of the multi-crystalline silicon texturing process.

Staining and incomplete rinsing have been reported (8), caused by inadequate processing, most likely by incomplete and inadequate removal of the porous silicon and chemical residue remaining on the wafer. Successful processing requires no staining caused by the poor removal of the porous silicon and other silicon-based compounds, such as nitrides or oxides that may be formed during the HF/HNO_3 acid texturing bath. Additionally, the chemical must be completely rinsed off the surface, leaving no streaks, residual chemicals, or other contamination.

(a)

HF/HNO_3 Acid Texturing	Rinsing	KOH Porous Si Removal	Rinsing	HF/HCl	Rinsing	SC-1 Surface Condition	Rinsing	Drying

(b)

HF/HNO_3 Acid Texturing	Rinsing	KOH Porous Si Removal	Dilute HF/HCl Rinsing	Dilute Oxidizing Proprietary Rinsing	Drying

(c)

HF/HNO_3 Acid Texturing	Dilute Proprietary Rinsing	Dilute HF/HCl Rinsing	Oxidizing Proprietary Rinsing	Drying

Figure 1. Schematics above show the process baths and rinses for (a) typical manufacturing texturing process, (b) proposed simplified process when a KOH or NaOH bath is used for removing porous silicon, and (c) proposed simplified process when porous Si removal is not used and the HF/HNO_3 solution must be rinsed prior to the wafers being placed in the HF/HCl bath because of surfactant addition.

Introduction

To reduce the cost of the entire texturing and surface conditioning process, the post-texturing chemical baths are eliminate and replaced with rinsing steps that use low concentrations of chemicals. The post-texturing alkaline bath is replaced with a hot water rinse or a rinse using an oxidizing agent. The post-texturing HF/HCl bath is eliminating and replaced with a HF/HCl rinse. The final SC-1 or oxidizing bath is replaced with a dilute SC-1 or NH_4OH rinse or a proprietary oxidizing rinse. The proprietary rinse forms a high-quality chemical oxide layer, which is advantageous for uniform emitter formation with wet-phosphorus doping. The final rinses adequately remove the post-texturing contaminants, including the porous silicon and remnants of the surfactant, if used, and leave the wafer with a uniform hydrophilic surface.

The proprietary rinse water can be used after the HF/HCl rinse and is also recycled to be used again after the HF/HNO_3 or prior baths. Figure 1(b) and 1(c) show the proposed simplified texturing and post-process flows. This simplification was derived from the dilute chemical baths that are used for surface conditioning of semiconductor wafers (9).

Experimental

Both vertical wafer orientation using batch immersion and horizontal roller in-line tools are used for PV manufacturing. For this study, a batch immersion processing tool is used, the MTS Orca prototype, which provides a throughput of over 1500 wafer per hour for the standard 30 MWp configuration (10). The tanks are equipped with filtration and pumping capability, plus bleed-and-feed and chemical balancing capability for maintaining constant concentration, especially for the HF/HNO_3 texturing bath. An airknife removes chemicals from the wafers before the rinsing baths to minimize chemical carry-over. The rinsing baths use cascade overflow technique. Chemicals are spiked into the rinsing water.

High purity, semiconductor grade chemicals are used, although solar grade chemicals can also be used. Deionized water (DI H_2O) at approximately 15 MΩ·cm is used.

The texturing baths tested used HF/HNO_3 with H_2O, acetic acid, phosphoric acid, and surfactant at various ratios to test the ability to rinse these chemicals. Acidic texturing bath formulations and temperatures similar to the published ECN and UKN processes were evaluated to show that the chemicals could be effectively rinsed. Not all bath formulations were thoroughly tested for their texturing capability.

Wafers used are low resistivity, p-type, 156 × 156 mm^2, either 200 or 180 μm thick. Saw damage is apparent on some wafers.

Results

Process

Results show that the proposed simplified rinsing process flow achieves the same results as the concentrated chemical baths. There is no change to the texturing topology, reflectivity, or doping uniformity. In both cases the saw damage is removed. The target thickness removal of silicon is 9.0 μm, approximately 4.5 μm evenly distributed on both sides of the wafer.

Figure 2(a) shows a micrograph of the textured silicon surface with the standard concentrated bath process at high magnification showing the textured porous-looking surface and Figure 2(b) shows the surface after the dilute HF/HCl and dilute SC-1 rinse. There is no change in the texturing topography. The porous silicon layer is removed and the roughen silicon surface is observed for both processes. Figure 3 is a micrograph of the textured silicon surface at higher magnification, showing the micro-roughness that increase the surface area, thus allowing less reflection of light.

There is no degradation of reflectance with the simplified process. Figure 4 shows the reflectance after the texturing and surface conditioning process using full-strength chemical baths and after rinsing with dilute chemicals. The reflectance at 950 nm is <17% with both the concentrated chemical baths with rinses and the simplified process

using dilute HF/HCl and SC-1 rinses after the NaOH bath. The full reflectance spectrum shows that there is little difference at any of the wavelengths measured.

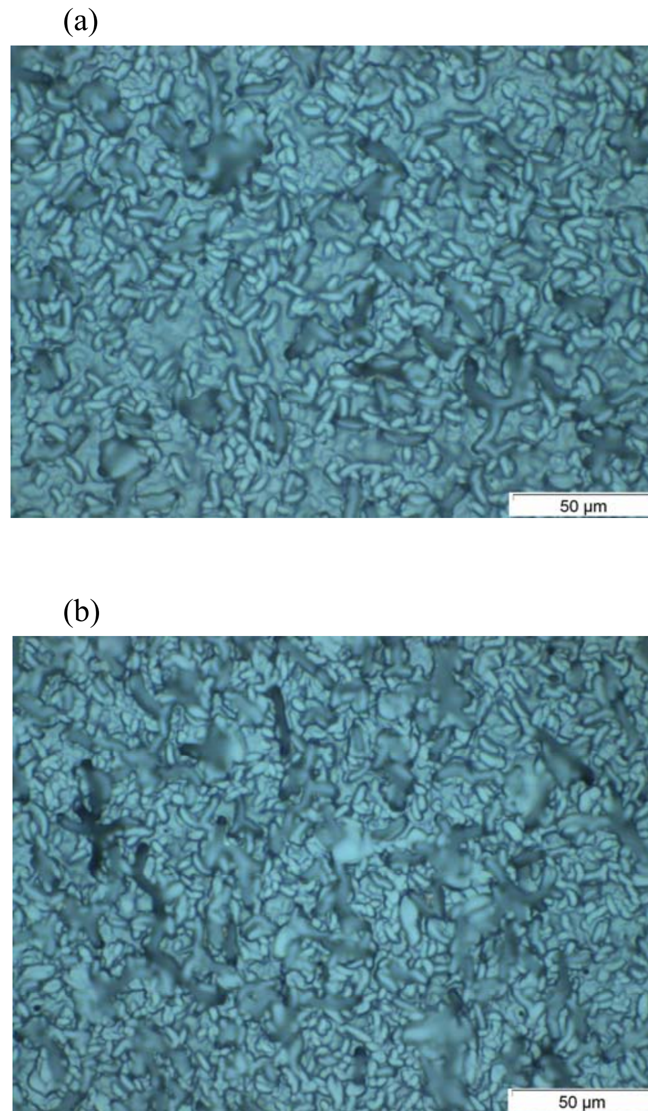

Figure 2. Micrographs of the surface of multi-crystalline silicon wafers processed with (a) standard high-concentration baths and water rinses and (b) proposed simplified dilute HF/HCl and SC-1 rinse processes after the HF/HNO_3 and NaOH alkaline bath.

Various concentrations of HF/HCl rinsing solution are tested ranging from concentrated 1:0.025:10, 1:0.0025:1000 $HF:HCl:H_2O$. Even more dilute solutions may be efficient. Rinse times were varied to determine the point at which the wafers were hydrophobic with a slight overetch, indicating the chemical oxide was completely removed. Solutions were tested with and without HCl to determine the effectiveness of removing the alkaline ions from NaOH.

The rinsing process reuses water in the following sequence. The water after the last rinsing cycle in the proprietary oxidizing bath reuses the rinsing water in the HF/HCl bath,

which in turn is reused as rinse water in the post-porous silicon removal bath or the proprietary post-acid texturing bath.

Results show that the oxide formed after the proprietary rinse give a hydrophilic surface. Although contact angle is not a good indication of wetting for the textured surface; a water droplet spreads uniformly and shows good wet-ability. The doping uniformity, as judged by the sheet resistivity, varies less than <2.2% across the wafer for SC-1, and the proprietary rinsing method.

Figure 3. Micrograph of the surface of multi-crystalline silicon wafers after texturing showing the roughness that allows increased surface area corresponding to increased light absorption and less reflectance.

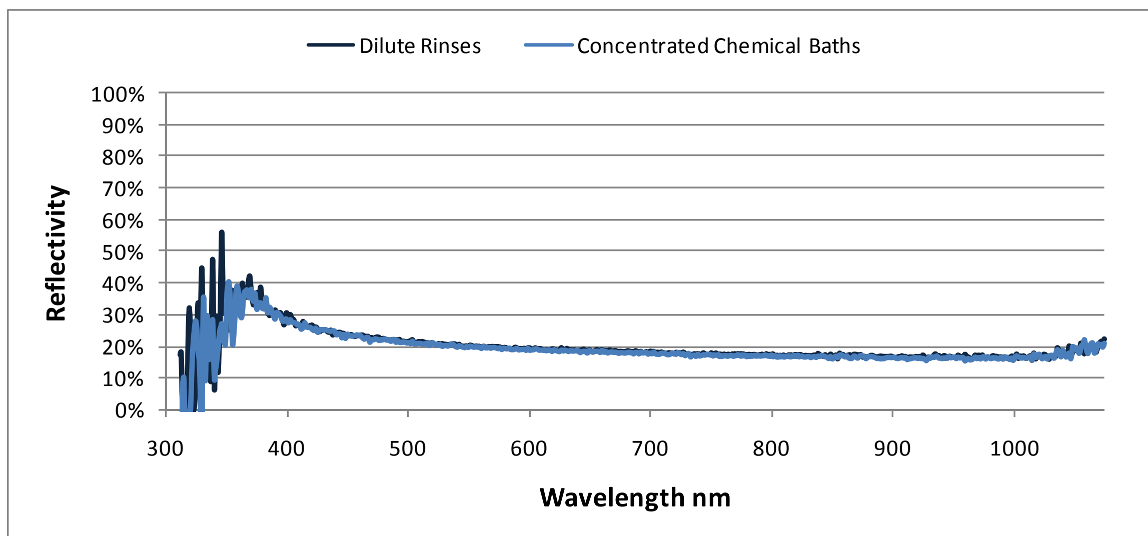

Figure 4. Reflectivity spectra comparison for multi-crystalline silicon wafers processed with concentrated chemical texturing and cleaning process and proposed simplified dilute chemical rinses.

Productivity

The rinse cycles have been optimized to minimize the amount of water. The proposed rinsing processes, with cascade overflow rinses coupled with the reduction of rinsing cycles, uses 45% less water than spray rinses. A texturing platform configured for vertical processing uses 9 rinsing tanks while the simplified process uses 6 rinsing tanks, two with chemicals, as shown in Table I. Also, Table I shows the amount of rinse water saving as a result of the sequential reuse of chemicals based on a 5 minute rinse in each DI H_2O or diluted chemical tank.

Flow rates for rinsing can vary from 1 up to 20 liter/min, depending on the chemical being rinsing. Therefore, using simplified calculations, the typical texturing tank at 10 liters per minute uses $9 \times 10 \times 5 = 450$ liters per process cycle with no recycling, while the simplified process uses $6 \times 10 \times 5 = 300$ liters per process cycle with no recycling or $4 \times 10 \times 5 = 200$ liters per process cycle for bath loads of approximately one hundred 156×156 mm^2 silicon solar cell substrates. Thus, approximately a 33% to 55% savings of rinsing water with the simplified process can be obtained.

The dual tank cascade rinse configuration adequately distributes the rinsing solution over the tightly-packed immersed wafers to quickly remove the process chemicals. The acid baths that had surfactant added proved the most difficult to rinse effectively. The rinse baths with chemicals were designed to need no intermediate rinse.

Additionally, the rinse cycle throughput is designed to be compatible with the texturing bath to optimize throughput and station the wafers throughout the process to minimize the time the bath is not in use; process times to match the acid bath were not difficult to achieve. Adequate rinsing was achieved in less time than the process, as shown in Table II. However, depending on the HF concentration, the rinse time can vary; a more dilute HF solution requires a longer rinse time, depending on the etch rate of chemical oxide that is achieved with the concentration used. Depending on the texturing processing time, multiple processing tanks can be used, coordinating the rinsing cycle time with the chemical processing time.

Table II shows the time reduction for the processes by reducing the number of tanks and process steps; a greater than 25% improvement in processing time is realized. Additional throughput improvement can be made by having multiple acid and alkaline process tanks that operate sequentially or in series to balance the rinsing cycles.

In addition to reduction of time and chemical, the footprint of the tool is reduced to approximately 20% less than the full ECN-based, concentrated chemical, process tool; from approximately 1500 cm to less than 1200 cm in length due to the elimination of chemical and rinsing process tanks.

The surface conditioning and rinsing processes are compatible with thin wafers, using a proprietary wafer hold to keep the wafers flat and stable during the processing. A surface tension gradient dryer can also be used for the tightly spaced wafers or a standard air dry can be used.

Summary and Conclusions

In summary; concentrated baths after the texturing bath can be replaced with dilute chemical rinsing processes. The concentrated HF/HCl bath has been replaced with a low-concentration rinse, which effectively removes any sodium ions from the alkaline bath

and also leaves the surface hydrophobic to allow uniform oxidation from the dilute SC-1 bath. A propriety rinse has been proposed that oxidizes the surface that can replace the SC-1 rinsing bath. The entire process sequence has been simplifies by eliminating the HF/HCl and oxidizing baths and replacing each with a simplified rinsing steps. Results are equivalent to the concentrated process, such as the ECN or UKN process, and also achieve a faster throughput, lower cost, and smaller footprint.

TABLE I. Comparison of Water Usage

Concentrated Process			**Simplified Process**		
Step	**Number of Rinsing Tanks**	**Volume Used (Liters)**	**Step**	**Number of Rinsing Tanks**	**Volume Used (Liters)**
HF/HNO_3 Rinse	2	100	HF/HNO_3 Rinse	2	100
Alkaline Rinse	2	100	Alkaline Rinse	2	100
HF/HCl Rinse	2	100	Dilute HF/HCl	1	50
Oxidizing Rinse	2	100	Proprietary Rinse	1	50
Final Rinse	1	50			
TOTAL	**9**	**450**	**TOTAL**	**6**	**300**

TABLE II. Comparison of Process Times

Concentrated Process		**Simplified Process**	
Step	**Process Time (Minutes)**	**Step**	**Process Time (Minutes)**
HF/HNO_3 Bath	20	HF/HNO_3 Bath	20
Rinse	5	Rinse	5
Alkaline Bath	20	Alkaline Bath	20
Rinse	5	HF/HCl Rinse	5
HF/HCl Bath	5	Proprietary Rinse	5
Rinse	5	Dry	2
Oxidizing Bath	10		
Rinse	5		
Dry	2		
TOTAL	**77**		**57**

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