# GEORGIA TECH &

# AIR PRODUCTS

## PRE-TEXTURE CLEAN

## FINAL REPORT

Georgia Institute of Technology

2106ACS

# Georgia Tech – Air Products

*Final report*

The use of cleaning chemistry, SunSource™68 developed by Air Product Chemicals, Inc. (APCI) to control random texturing time and pyramid size on mono-crystalline silicon wafers. This chemistry is applied immediately after saw damage removal, which removes residues and acts as a catalyst to initiate texturing very rapidly. Due to rapid nucleation, the amount of IPA needed in the solution is very small and our texturing time is cut down by half. Thus the amount of silicon removed as a result of texturing is ~45% less than the standard texturing without the clean and this increases the texturing bath life. We have applied this cleaning chemistry before texturing and compared with the standard texturing process. The use of the cleaning solution has produced uniform pyramids across a wafer and from wafer to wafer, irrespective of wafer vendor. We found, repeatedly and reproducibly, ~0.5% efficiency improvement with the cells made in conjunction with the cleaning chemistry. This improvement resulted from a combination of lower weighted reflectance and narrow gridlines resulting from uniform and small pyramids associated with the cells using cleaning chemistry. We have demonstrated an 18.3% average efficiency large area (239 cm2) cells on 2.6 Ω-cm CZ Si compared to 17.8% for the standard textured cells.

INTRODUCTION

One of the challenges in maintaining high yield in the solar cell industry is the reliability of front surface texturing to achieve, consistently and reproducibly, pyramid sizes of choice. This is due to incomplete cleaning immediately after wafering, which leaves some residue on the wafer surface. These residues are not completely removed during the saw damage removal step and can lead to non-uniform texturing. The type and amount of residue varies from one wafer vendor to another depending on their particular cleaning process post-wafering. Most often, the texturing has to be optimized according to the wafer vendor and often results in

uncertainty of the texturing time and final pyramid size. Not only is the wafer surface texturing the key to reducing reflectance on solar cells, it is also critical to the front metal contact printing. Therefore it is important to optimize this unit process to improve yield. The standard surface texturing is normally effected in an alkaline solution for mono crystalline wafers after saw damage removal. The duration in the texturing solution is a function of temperature and the wafer source. Depending on the wafer source, texturing can be non-uniform because of the residue left on the wafers after wafering. In order to circumvent the uncertainties and control texturing a preclean chemical was proposed to remove any residue prior to texturing step. In this work we investigated the efficacy of cleaning chemistry, SunSource™68, developed by APCI on silicon wafer texturing as compared to the standard texturing process without cleaning. We started with surface analysis to understand the finger prints of the residue left on the wafer after sawing and cleaning. We applied the cleaning chemistry after saw damage removal and then textured the wafers and compared results with no clean chemistry case. We then fabricated and characterized solar cells.

Incoming wafer surface analysis

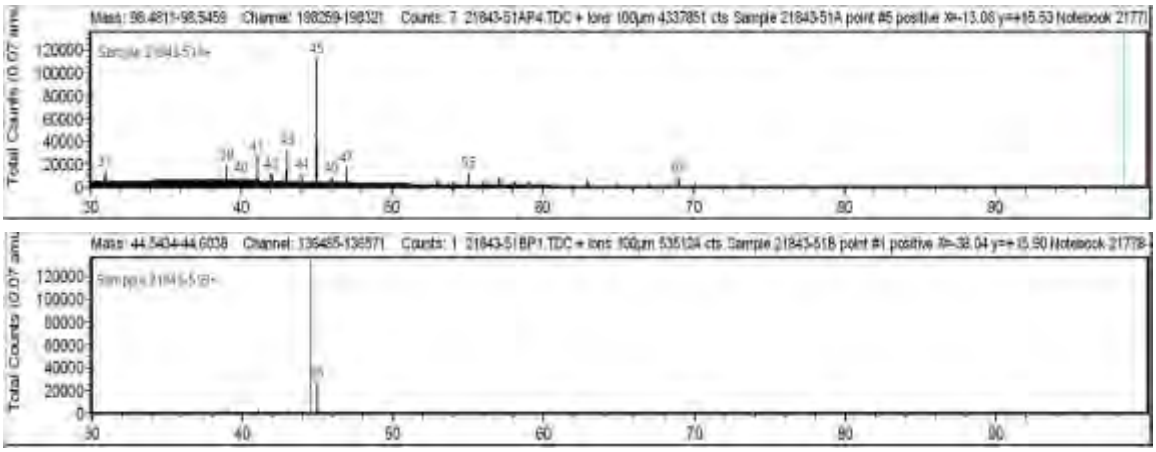


**Figure 1: Positive SIMS surface analysis showing incoming wafer cleanliness from suppliers DSMO and SOMO**

Incoming wafer surface analysis shown in Figure 1 compares the incoming wafer surface cleanliness from two wafer suppliers. The surface cleanliness from these two wafer suppliers is significantly different. The peak at 45 corresponds to stearamide, a lubricant used during sawing. This residue affects the saw damage removal and texturing steps.

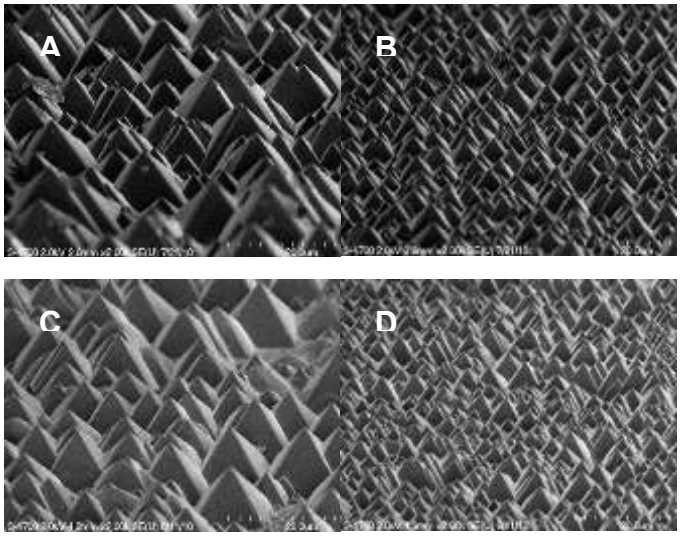


**Figure 2: (A) No clean (B) with clean chemistry –Vendor A; (C) No clean (D) with clean chemistry –Vendor B.**

Figure 2 shows the textured surface on wafers with and without cleaning with SunSource™68. The wafer without cleaning (Figure 2A from vendor A) shows a wide distribution of pyramid sizes, which is not desirable. Wafer subjected to cleaning for 5 minutes at 70oC after the saw damage removal step (Figure 2B from vendor A) shows very uniform distribution of smaller pyramids. The same effect was observed with wafers from vendor B (Figs. 2C and 2D). Note that the magnification is the same for all images.

Process sequence with cleaning

**Table 1: Silicon etch rates during texturing**

| | Average etch rate during texturing (mm/min) | Standard Deviation |
|---|---|---|
| Saw damage etch + Texturing (no clean) | 0.86 | 0.06 |
| Cleaning + Saw damage etch + Texturing | 0.60 | 0.01 |
| Saw damage etch + Cleaning + Texturing | 0.43 | 0.02 |

The silicon etch rate during texturing was investigated as shown in Table 1. The result indicates the application of the cleaning chemistry prior to saw damage removal gives slightly lower etching rate than without cleaning. However, when the clean chemistry is applied after saw damage removal, the etch rate is slow and results in a more uniform and smaller pyramids. Based on these result, the process sequence was set at saw damage removal followed by cleaning followed by texturing.

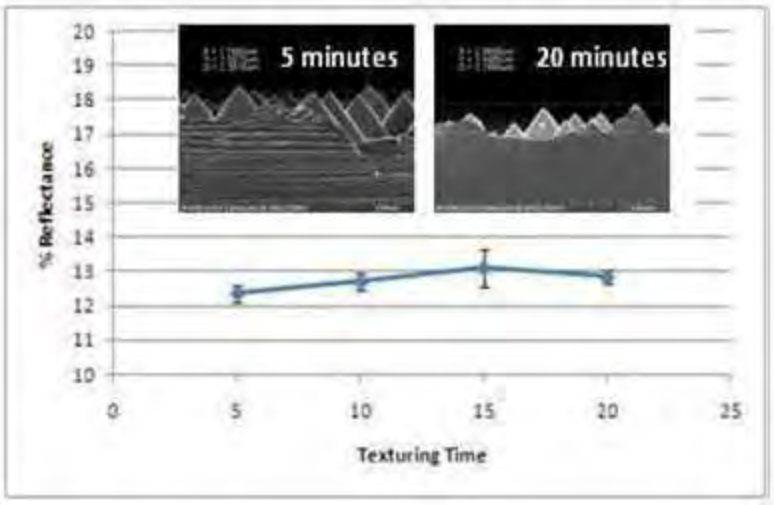


**Figure 3: Effect of texturing time (minutes) on wafer surface reflectance (saw damage etch → clean → texture).**

Figure 3 shows the effect of texturing time on reflectance. As shown in the insert, the 5 and 20 minutes texturing did not show any appreciable difference in pyramid size or reflectivity. This indicates the process reliability can be greatly improved, since the pyramid structure is not dependent strongly on process times. This is particularly important for throughput if texturing time can be reduced to only five minutes without compromising the reflectance. Similar observations were made for texturing of silicon wafers from several vendors.

## CELL FABRICATION

After the cleaning process was optimized we applied the following cell fabrication sequence. Fifty 239 $cm^2$ Cz (~2 Ω-cm) went through saw damage removal. Half received the SunSource™ 68 surface clean before texturing. All wafers were diffused in a POCl3 furnace for a final sheet resistance of 65 Ω/sq. After removal of phophosilicate glass and chemical edge isolation, the wafers received a single layer 80 nm SiNX antireflective coating via low frequency plasma enhanced chemical vapor deposition. All wafers were contacted by screen-printing front Ag gridlines and Al back contacts, each print followed by drying at 200°C for 2 minutes. All wafers were co-fired in an IR belt furnace followed by light IV testing, etc.

## RESULTS AND DISCUSSION

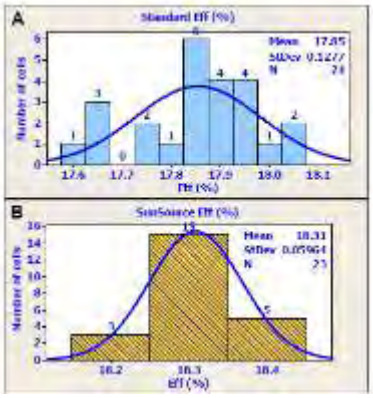


**Figure 6: (A) Efficiency for cells with standard texturing (no cleaning); (B) Efficiency for cells with SunSource™68 cleaning.**

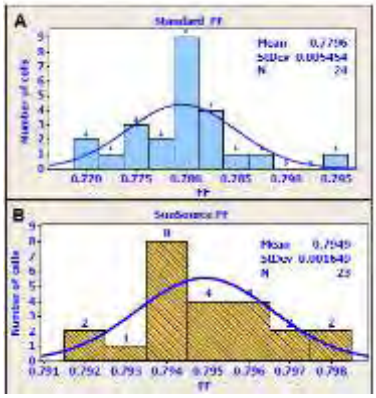


**Figure 7: Fill factor comparison for the (A) standard and (B) cleaned cells.**

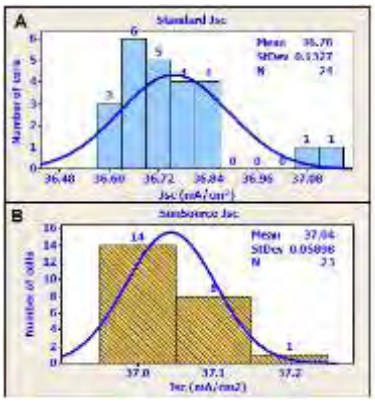


**Figure 8: Short circuit current comparison for the standard (A) and cleaned (B) cells.**

Figure 6 compares the efficiency of cells fabricated with the standard texturing and cleaning before texturing. The cells with cleaning show a tighter distribution than the standard texturing. Average efficiency of 18.31% compare to 17.85%.

The average short circuit current (Figure 7) and fill factor for the cleaned cells were superior to the standard counterparts due to difference in reflectance (Figure 8).

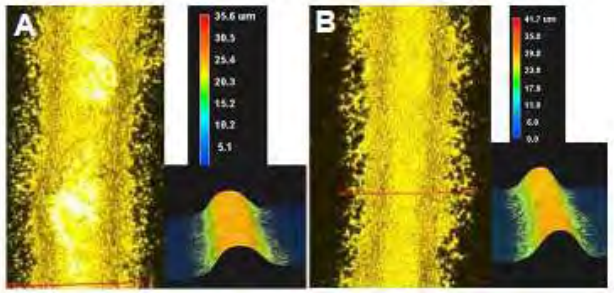


**Figure 9: (a) SunSource™68 cleaned cells with average line width of ~123 μm and 25 μm average height (b) Average line width of ~143 μm and 25 μm line height for standard cell.**

Figure 9 shows the gridline geometry for the cleaned and standard cells. Although the gridlines on both cells had the same average line height, their width was ~20 μm different in favor of the cleaned cells. The wider lines for the standard cells could be due to non-uniform pyramids which results from the residue on the incoming wafers. However, the cleaning chemistry removes this residue and facilitates the nucleation and texturing of wafers with greater control on pyramid size. The controlled pyramid size promotes less spreading and resulted in narrower fingers.

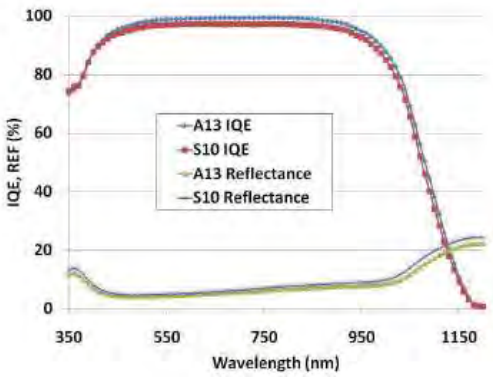


**Figure 10: IQE and reflectance for APCI clean (A13) and standard (S10) cells.**

Figure 10 compares the internal quantum efficiency (IQE) and the reflectance for cleaned (A13) and standard cells (S10). The short wavelength response for the two samples is similar

because the same emitter was used. The reflectance is slightly different, probably due to the difference in line width in addition to smaller and uniform pyramids for the cleaned cells.

Front surface recombination velocity (FSRV) and back surface recombination velocity (BSRV) values, for the two cells, were extracted by matching the measured short and long wavelength responses with the PC1D calculated response. From this calculation, the FSRV, BSRV and the bulk lifetime are found to be the same, 1.2E5 cm/s, 320 cm/s and 300 µs, respectively. However, we observe some variation in the front and back surface reflectance (BSR) by 0.3% and 4%, respectively, which is responsible for the higher JSC difference between the cleaned and standard cells.

## CONCLUSIONS

We have investigated the use APCI SunSource™68 pretexture clean and texturing to circumvent the uncertainty in alkaline texturing of mono crystalline silicon wafers. The clean is effective in removing residue left from ingot sawing, irrespective of wafer vendor, and initiate texturing instantaneously. This enables complete and uniform texturing of mono crystalline in a shorter time than the standard. Thus, the pyramid size can be controlled. It was also observed that the pyramid size did not increase appreciably with increasing texturing time, which gives greater control over the process.

By applying the pre-texture clean to cell fabrication, the efficiency was higher by ~0.5%, (average) than cells with standard texturing (no clean). Although the FSRV, BSRV and carrier lifetimes were the same, the difference in the efficiency was mainly due to a 0.3% front reflectance and 4% BSR.

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# THE IMPACT OF SURFACE CLEANING ON RANDOM TEXTURING OF CRYSTALLINE SILICON WAFERS

ABSTRACT: In this paper we report on the use of a cleaning solution, SunSource™ 68, formulated by Air Product and Chemicals, Inc., which produced uniform pyramids across a wafer and from wafer to wafer. The use of this chemical reduced the texturing time to about one half the time compared to standard texturing. The pre-texture clean with SunSource™ 68 reduces the dependence of texturing on the amount of IPA in the texturing bath. We found, repeatedly and reproducibly, an efficiency improvement with the cells made in conjunction with the cleaning chemistry. This improvement resulted from a combination of lower weighted reflectance and narrow gridlines resulting from uniform and small pyramids associated with the cells using SunSource™ 68. The cells with cleaning showed a tighter distribution than the standard texturing. Average efficiency of 18.41% on large area (239 $cm^2$) cells 2.6 Ω-cm CZ Si compared to 18.27% for the standard textured cells have been demonstrated. Best efficiency of 18.5% and 18.3% were obtained for the SunSource™68 pre-clean and standard cells, respectively.

# 1 INTRODUCTION

Reducing the surface reflectance is key to increasing absorption and hence efficiency of a solar cell. However, in the solar industry, it is challenging to maintain high yield and reliability of front surface texturing to achieve, consistently and reproducibly, uniform pyramid sizes of choice. Incomplete cleaning immediately after wafering, can leave residue on the wafer surface that cannot be cleaned readily by KOH during saw damage removal, which is the first step before texturing. Because these residues are not completely removed during the saw damage removal step, when the wafers are placed in texturing solution, it will cause non-uniform nucleation and texturing. The type and density of residue varies from one wafer vendor to another depending on their particular cleaning process after wafering. Because of the uncertainty of the type and density of residue, texturing has to be optimized according to the wafer vendor, which often results in uncertainty of the texturing time and pyramid uniformity and size. To take control of texturing time, pyramid size and uniformity, while improving yield and cell efficiency, a cleaning chemistry, SunSource™ 68, has been developed by Air Product and Chemicals, Inc., to remove the surface residue before texturing. This chemistry is applied immediately after saw damage removal, which removes residues and initiates texturing very rapidly. Due to rapid nucleation, the amount of IPA needed in the solution is very small and texturing time can be reduced. Therefore, the amount of silicon removed as a result of texturing is less than the standard texturing and thus can prolong the texturing bath life. In this paper we investigated the efficacy of SunSource™68 on silicon wafer texturing as compared to the standard texturing process without cleaning. In particular, we investigated texturing time, pyramid size, the amount of IPA needed to achieve excellent texturing and the texturing bath life compared to the standard bath without SunSource™ 68. We also made solar cells on textured samples utilizing the SunSource™ 68 before texturing and compared to those with standard texturing without the clean.

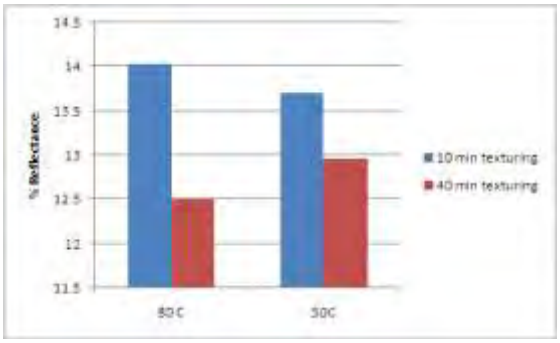


**Figure 1:** Reflectance as a function of cleaning tempererature for 10 and 40 minutes texturing

In our previous work [1] we reported that the surface analysis of an incoming wafer showed stearamides remaining on a wafer surface after post-wafering clean. These compounds represent some of the residues that cause non-uniform saw damage removal and leads to poor texturing. However, the application of SunSource™ 68 immediately after saw damage removal removes these residues (irrespective of wafer vendor) and enables texturing to commence instantaneously. This cleaning step is done at temperature higher than the room temperature. In order to determine the effect of clean temperature on the efficacy of the clean chemistry, we investigated two cleaning temperatures, 50°C and 80°C, before texturing. For each cleaning temperature we investigated the texturing times of 10 and 40 minutes.

Figure 1 shows the reflectance at the two cleaning temperatures for 10 and 40 minutes texturing. The weighted reflectance of ~14% was measured for the 80°C cleaning temperature for 10 minutes, but slightly lower for the 50°C. As the texturing time increases, the weighted reflectance decreases to 12.5% for the 80°C temperature and >12.5% for the 50°C.

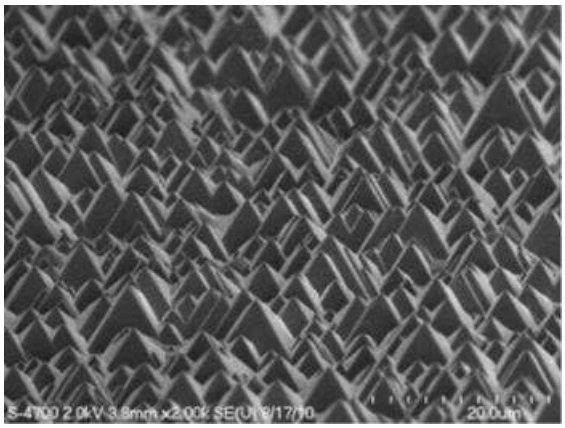

**Figure 2a:** SEM micrograph of 10 minutes texturing and 50°C cleaning

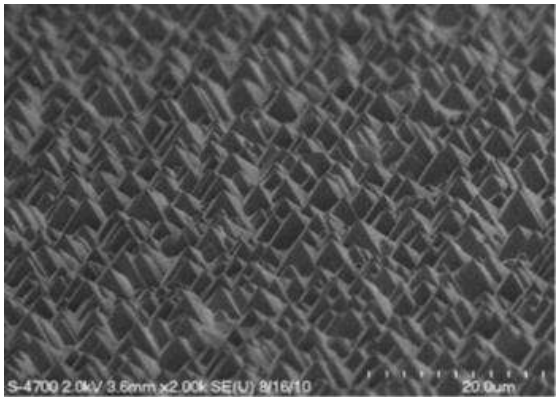

**Figure 2b:** SEM micrograph of 10 minutes texturing for 80°C cleaning

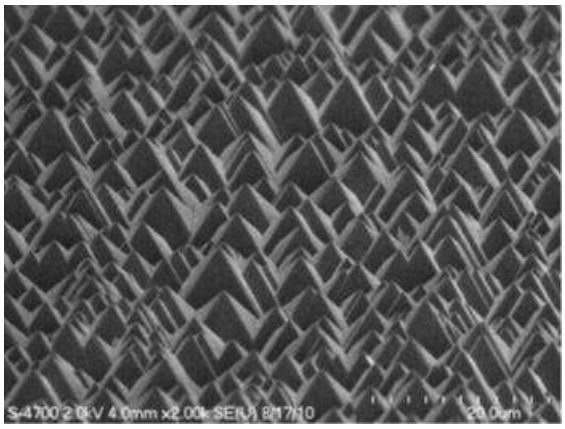

**Figure 3a:** SEM micrograph of 40 minutes texturing for 50°C cleaning

Figure 2a and 2b show the SEM micrographs of the surfaces after 10 minutes texturing at 50°C and 80°C cleaning, respectively. The micrographs are very similar and show some non-textured sites. This is why the weighted reflectance for the two cases is high.

Figure 3a and 3b show the SEM micrographs of the surfaces after 40 minutes texturing at 50°C and 80°C, respectively. The micrographs are very similar and show complete texturing. This is why the weighted reflectance for the two cases is similar and lower than the 10 minutes texturing cases.

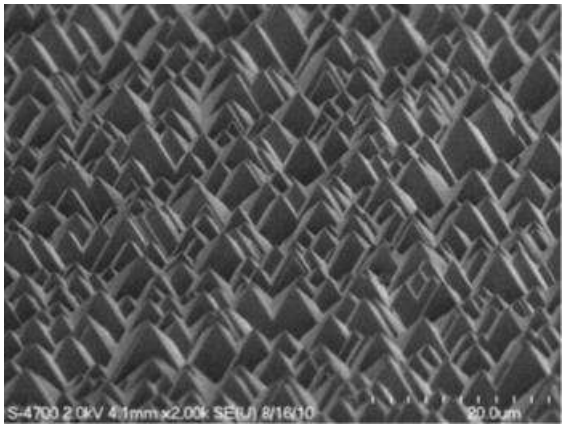

**Figure 3b:** SEM micrograph of 40 minutes texturing for 80°C cleaning

The results in figures 2 and 3 were textured in 1-2% KOH solution with 3% IPA. In order to ascertain the effect of IPA concentration in texturing bath, we varied the IPA percentage and measured the weighted reflectance with and without prior cleaning with SunSource™ 68. Figure 4 compares the effect of IPA on a 40 minutes texturing for wafers that had the clean and without the clean. These experiments were performed on wafer pieces in beaker level tests.

Figure 4: Effect of IPA on wt average reflectivity with and without cleaning

Figure 4 shows that the reflectance for the wafers with pre-clean before texturing is essentially independent of the percentage of IPAin the texture bath. For to the standard process with no prelceaning, the reflectance decreases sharply with increasing IPA percentage. These results indicate that precleaning substantially improves process stability so that variations in IPA level in the texture bath will have minimal impact on texturing.

Next we investigated the texturing bath life and the result is shown in Figure 5. The texturing time per batch for the standard process was 40 minutes, which is minimum required to obtain complete texturing without precleaning. With the SunSource™ 68 clean step, the texturing time was reduced to 20 minutes per batch. From Figure 5, it is evident that the cleaning process results in reflectance consistently below 12.6% for the 12 wafer batches, at which point the experiment was stopped. Without the clean step, the reflectance values are consistently above 13%. Figure 6 shows the silicon concentration in the texture bath versus number of wafers processed. The silicon concentration increases at a much slower rate when the SunSource™ 68 is used, which allows for extended texture bath life with the preclean. From these results, it can be concluded that the SunSource™ 68 clean is capable of removing redsidues and initiating texturing immediately after the wafers are placed in the texturing bath. In addition, because of this rapid nucleation, the amount of silicon removed is less than the standard as shown in Figure 6. Because of this instantaneous nucleation and texturing, the pyramid size is tightly controlled as shown in Figures 7a and 7b. Figure 7 shows the SEM micrographs of wafers textured for 5 and 20 minutes. There is very little or no difference in pyramid size for the two cases.

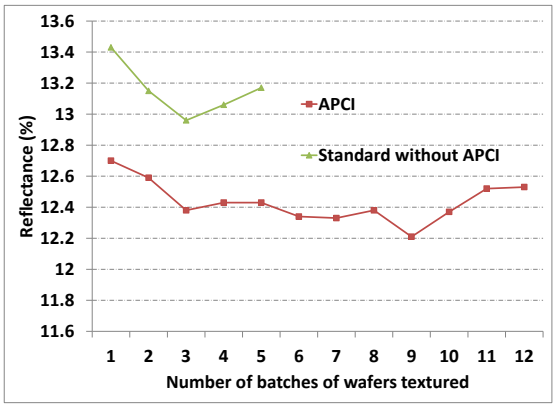


Figure 5: Reflectance as a function of number of batches of textured wafers

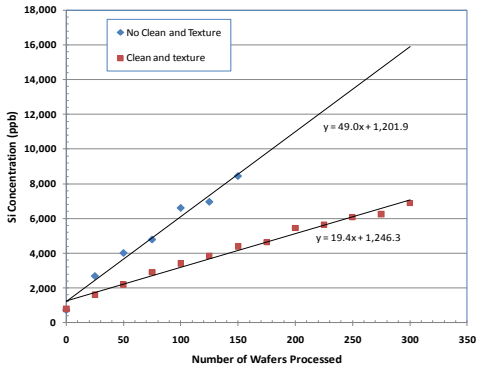


Figure 6: Si concentration in texture bath as a function of number of wafers processed: No clean and with clean.

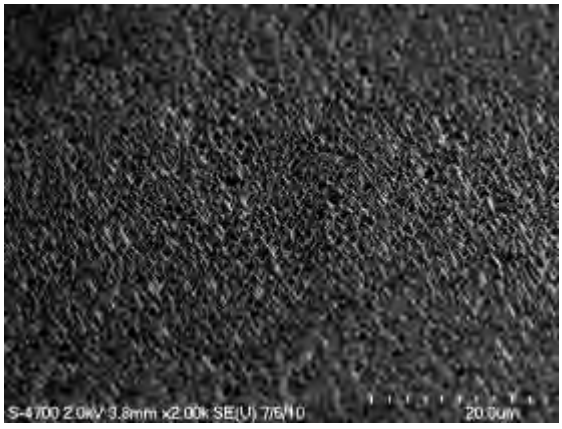

Figure 7a: 5 minutes texturing after pre-clean in SunSource™ 68

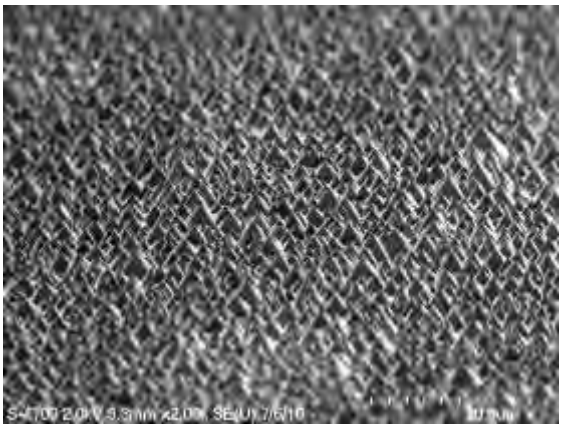

Figure 7b: 20 minutes texturing after pre-clean in SunSource™ 68

## 3 CELL FABRICATION

After the cleaning process was optimized we applied the following cell fabrication sequence. Fifty 239 $cm^2$ Cz (~2 Ω-cm) went through saw damage removal. Half received the SunSource™ 68 surface clean before texturing. All wafers were diffused in a $POCl_3$ furnace for a final sheet resistance of 65 Ω/sq. After removal of phosphosilicate glass and chemical edge isolation, the wafers received a single layer 80 nm $SiN_X$ antireflective coating via low frequency plasma enhanced chemical vapor deposition. All wafers were contacted by screen-printing front Ag gridlines and Al back contacts, each print followed by drying at 200°C for 2 minutes. All wafers were co-fired in an IR belt furnace followed by light IV testing, etc.

## 4 RESULTS AND DISCUSSION

**Table I:** LIV data showing average and best parameters for standard cells without SunSource™ 68 clean

| Cell Id | $V_{OC}$ (mV) | $J_{SC}$ (mA/cm²) | FF (%) | Eff (%) | n-factor | Rs (Ωcm²) |
|---|---|---|---|---|---|---|
| Av. | 627 | 37.0 | 78.8 | 18.27 | 1.04 | 0.68 |
| Best | 628 | 37.0 | 78.9 | 18.30 | 1.05 | 0.68 |

**Table II:** LIV data showing average and best parameters for cells with SunSource™ 68 clean

| Cell Id | $V_{OC}$ (mV) | $J_{SC}$ (mA/cm²) | FF (%) | Eff (%) | n-factor | Rs (Ωcm²) |
|---|---|---|---|---|---|---|
| Av. | 627 | 37.3 | 78.7 | 18.41 | 1.04 | 0.70 |
| Best | 628 | 37.3 | 78.8 | 18.50 | 1.05 | 0.65 |

Tables I and II compare the electrical parameters for cells fabricated with the standard texturing and cleaning with SunSource™ 68 before texturing. The cells with cleaning show a tighter distribution (not shown in tables), than the standard texturing. Average efficiency of 18.41% compare to 18.27%. The average short circuit current for the cleaned cells was superior to the standard counterparts due to difference in reflectance (Table III).

Figure 8 shows the gridline geometry for the cleaned and standard cells. Although the gridlines on both cells had the same average line height, their width was ~20 μm different in favor of the cleaned cells. The wider lines for the standard cells could be due to non-uniform pyramids which results from the residue on the incoming wafers. However, the SunSource™ 68 removes this residue and facilitates the nucleation and texturing of wafers

with greater control on pyramid size. The controlled pyramid size promotes less spreading and resulted in narrower fingers.

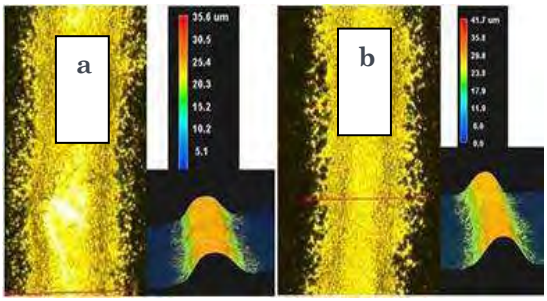


Figure 8: (a) SunSource™ 68 cleaned cells with average line width of ~123 µm and 25 µm average height (b) Average line width of ~143 µm and 25 µm line height for standard cell.

**Table III:** Comparison of best SunSource™ 68 cleaned and Std cells weighted reflectance

| Cell Id and description | Weighted reflectance (%) |
|---|---|
| Cleaned best cell (including metal) | 8.02 |
| Std best cell (including metal) | 9.14 |
| Cleaned No metal + SiN + Anneal | 7.13 |

4.1 Internal Quantum Efficiency (IQE)

Figure 9 compares the internal quantum efficiency (IQE) and the reflectance for SunSource™ 68 cleaned and standard cells (Std best cell). The short wavelength response

for the two samples is similar because the same emitter was used. The reflectance is slightly different, probably due to the difference in line width in addition to smaller and uniform pyramids for the cleaned cells.

Front surface recombination velocity (FSRV) and back surface recombination velocity (BSRV) values, for the two cells, were extracted by matching the measured short and long wavelength responses with the PC1D calculated response. From this calculation, the FSRV, BSRV and the bulk lifetime are found to be the same, 1.2E5 cm/s, 320 cm/s and 300 μs, respectively. However, we observe some variation in the front and back surface reflectance (BSR) by 0.3% and 4%, respectively, which is responsible for the higher $J_{SC}$ difference between the cleaned and standard cells.

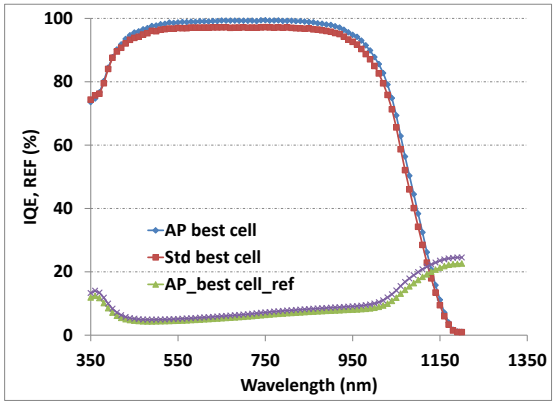


Figure 9: IQE and reflectance for SunSource™ 68 cleaned (AP best cell) and standard (Std best cell) cells.

## 5 CONCLUSIONS

We have investigated the use SunSource™ 68 pre-texture clean and texturing to circumvent the uncertainty in alkaline texturing of mono crystalline silicon wafers. The clean is effective in removing residue left from ingot sawing, irrespective of wafer vendor, and initiate texturing instantaneously. This enables complete and uniform texturing of mono crystalline in a shorter time than the standard. Thus, the pyramid size can be controlled even with the least amount of IPA in the texturing solution. It was also observed that the

pyramid size did not increase appreciably with increasing texturing time, which gives greater control over the process.

By applying the pre-texture clean to cell fabrication, the efficiency was higher by ~0.14%, (average) than cells with standard texturing (no clean). Although the FSRV, BSRV and carrier lifetimes were the same, the difference in the efficiency was mainly due to a 0.3% front reflectance and 4% BSR.