

IN-LINE AND VERTICAL TEXTURING OF MONO-CRYSTALLINE SOLAR CELLS

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ABSTRACT

Potassium Hydroxide (KOH) and Isopropanol (IPA) are currently being used to texturize and reduce the reflectivity of mono crystalline (mono-c) silicon wafer surfaces during the manufacturing of solar cells. One concern with this process is that the IPA is volatile which can lead to high replenishment rates, poor process stability, and increased costs. The flammable nature of the IPA should also be highlighted which can lead to handling and safety concerns. The goal of this work was to develop an IPA free process that does not compromise texturing or cell performance while providing improved process control. A secondary goal was to develop a chemistry that would allow for in-line texturing of mono-crystalline substrates.

INTRODUCTION

One of the key steps during the manufacture of silicon solar cells is wafer texturing. There are two goals of the texturing step. The first goal is to etch a sufficient amount of silicon to remove any damage that may have resulted during the previous wafer sawing step. The second goal is to create topography on the wafer surface to minimize light reflection. Different chemistries are used for mono and multi crystalline silicon wafers. This paper will focus on the texturing of mono-c silicon.

Potassium Hydroxide (KOH) is a well known etchant for silicon substrates and is widely used during the manufacture of CMOS, MEM and photovoltaic devices.^{1,2} One of the main reasons why KOH is so popular is that it is selective to the <111> plane of the silicon crystal structure. As a result, it is possible to create pyramid shaped structures on mono-c substrates which are quite effective in reducing the amount of reflected light from the silicon surface³. Although KOH was the focus of this work, the findings and trends reported also apply Sodium Hydroxide (NaOH) processes as well.

In order to achieve a surface with low reflectivity, it is important that the pyramid shapes have a base width of approximately 3-8µm and that they are uniformly dispersed across the entire surface. KOH by itself does not usually provide the desired pyramid structures because the etch rate is typically too fast to allow for sufficient peak formation and selective etching along the <111> plane. Additives are typically required to reduce the etch rate which in turn aids with peak formation and

selective etching. The equation below describes the chemical reaction taking place during silicon removal in the presence of KOH.



It is important to note that one of the byproducts during the etching reaction is potassium silicate. If the potassium silicate is allowed to accumulate at the interface between the wafer surface and chemistry, then the silicate passivates the surface which inhibits pyramid nucleation.

Increasing KOH concentration will help offset the presence of silicate at the surface but the resulting etch rate will be too high to allow for peak formation while maintaining good etch selectivity to the <111> plane. Another method to allow for good peak initiation is through the use of additives. Additives can improve the surface tension/diffusion dynamics of the solution such that a sustainable etch of the silicon surface is maintained while inhibiting the etch rate sufficiently to allow for good pyramid formation⁴.

IPA is widely used in production as an effective additive for mono-crystalline wafer texture chemistry. However, IPA is a flammable substance (flashpoint < 12°C) which requires additional safety measures when handling. Typical mono crystalline texturing is conducted at process temperatures in the 70° C-80°C range which is quite close to the boiling point of IPA (82.4°C). As a result, the IPA evaporates quickly which leads to unstable process control and increased replenishment/costs. The high evaporation rate of IPA also makes this process incompatible with in-line texturing equipment configurations.

There have been numerous references published on alternative chemistries to the traditional KOH/IPA process used for texturing mono-crystalline wafers^{5,6}. However in most cases, the solution either does not eliminate the IPA completely or poses additional costs. The goal of this work was to develop an alternative additive to IPA which will provide the following benefits:

- Improved process stability
- Lower additive consumption
- Similar or improved reflectivity
- Shorter process times
- Ability to texturize with in-line or vertical equipment
- Environmentally safe solution compatible with existing waste treatment procedures

EXPERIMENTAL APPROACH

There are a number of variables that need to be considered when developing an effective additive replacement to IPA. Key variables include:

- surface tension
- molecular weight
- boiling point
- temperature stability
- aqueous KOH miscibility
- concentration
- environmental impact
- cost

Numerous chemical species were screened analytically and empirically to study the impact of these variables on silicon removal rate, etch uniformity, and reflectance. Promising candidates were then further evaluated in beaker scale experiments to confirm performance and to continue process optimization. The optimized additive was then chosen and installed in commercial scale equipment at the Fraunhofer ISE to validate cell performance against a control process. Wafers were also evaluated at Schmid GmbH to evaluate performance on in-line texturing equipment. All testing was done on standard cz mono-crystalline wafers (156mm x 156 mm, p-doped 1.0-3.0 Ωcm). Unless otherwise indicated, the conditions shown in Table 1 were used for experimental evaluations.

	IPA Process	New Additive
KOH g/L	40	40-60
IPA g/L	40	-
Additive g/L	-	3-6
Temperature °C	80	80-90
Time min	40	10-20

Table 1: Typical process conditions used during experimental evaluations

RESULTS

Additive Stability

Figure 1 shows the evaporation loss for the IPA and proprietary additive over a period of 2 hours. The results clearly show that after a period of 30 minutes (texturing batch times are typically between 20-30 minutes) approximately 75% of the IPA has evaporated. The new additive however shows a small loss of about 3% after 30 minutes and about 10% loss after two hours.

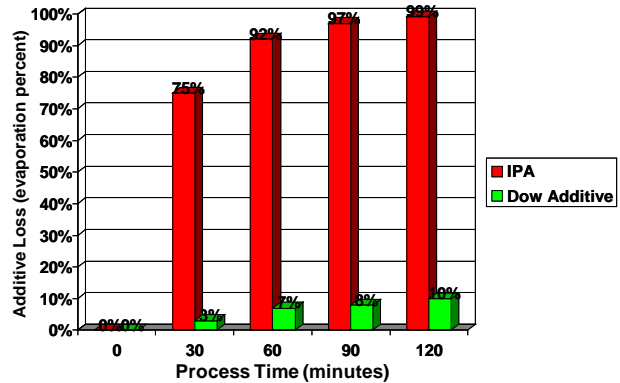


Figure 1: Additive Evaporation Loss (%) vs. Process Time

The evaporation loss has a significant impact on the process stability as shown in Figures 2 and 3. In the case of IPA, etch rate increases by nearly a factor of two as the IPA evaporates over a 30 minute period. This increase leads to less selective etching relative to the <111> plane thereby creating a more planar and reflective surface. The etch rate and reflectance achieved with the new additive remain constant up to two hours due to the significantly lower evaporation rate.

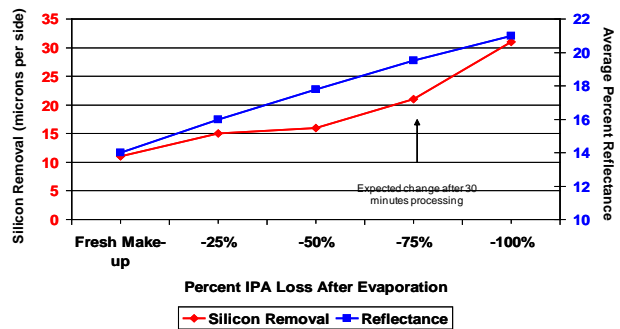


Figure 2: Impact of IPA evaporation loss on silicon removal and reflectance (360nm-750nm)

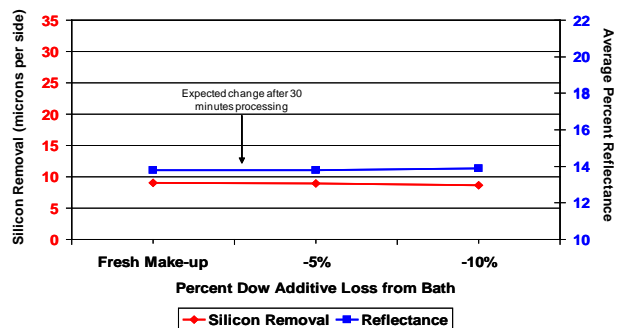


Figure 3: Impact of new additive evaporation loss on silicon removal and reflectance (360nm-750nm)

These results show that IPA will need constant replenishment to combat the effects of evaporation to provide a controllable process while the new additive will mostly require replenishment to compensate for chemistry dragout during processing. The additive is not consumed during the silicon etching reaction. Therefore, a key value proposition with the new additive will be reduced consumption of chemistry which will improve process cost of ownership.

Process Stability

In addition to the stability of the additive, there are a number of process parameters that should be considered to ensure sufficient performance under production settings. Such parameters can include the sensitivity of the additive to process temperatures, KOH concentrations, and silicate build up within a working bath. Figure 4 shows the impact of process temperature and time on silicon removal and reflectance for a given KOH concentration. As expected there is a small but manageable influence from temperature and time on etch amount but reflectance remains constant over the entire temperature/time range.

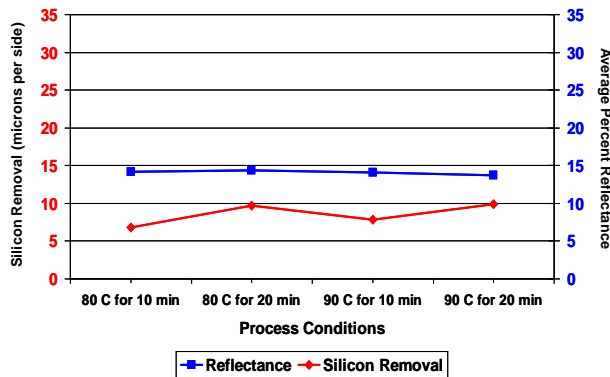


Figure 4: Impact of process temperature and time on silicon removal and reflectance (360nm-750nm)

The impact of potassium silicate build-up on texturing performance was approximated by texturing wafers in a 22L vertical tank without dumping the bath. It was assumed that the number of wafers per liter texturized on lab scale would reasonably translate to commercial size equipment. The maximum wafer/liter evaluated was 11.8 which is equivalent to approximately 2200 wafers for a 185 Liter process tank. Silicon removal and reflectance were measured for each wafer. Replenishment of the KOH was based upon the amount of silicon being etched plus dragout such that the hydroxide alkalinity of the bath was maintained. Replenishment of the additive was based upon the dragout amount only.

Figure 5 shows that over the course of the simulated 2200 wafers, the reflectance showed no significant trend despite an increase in K_2SiO_3 from 0 to 74.2 g/L. Although this

result needs to be confirmed on production scale, the data suggests that the additive is not sensitive to the amount of silicate in the bath and that potentially the bath life of the texturizer can be extended.

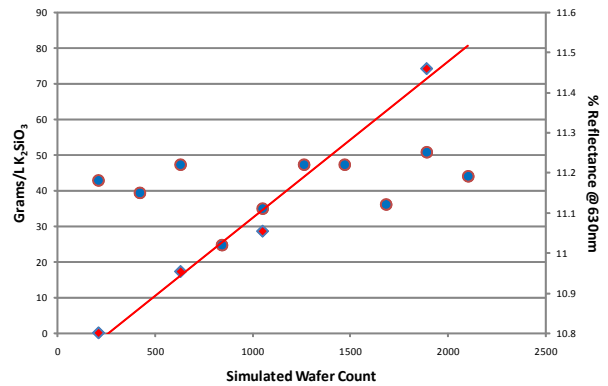


Figure 5: Impact of silicate formation on reflectivity (600nm). 60 g/L KOH, 6 g/L Additive at 80°C

Saw Damage Removal Vs. As Cut Wafers

Depending upon the production process flow, saw damage removal can be accomplished prior to the texturing step or in-situ with texturing. In the first case, KOH at concentrations of 10-20% are used to etch 5-15µm of silicon per side to remove any possible micro fractures which may have resulted from the wafering step. As mentioned earlier, these conditions typically produce wafers that have a planar surface due to the isotropic nature of the etch process. Wafers are then transferred into the texturing bath where a smaller amount of silicon is required to be removed to form the required pyramid peaks. The advantages of this process is that peak heights can be in the range of 2-5µm which may be preferable for the subsequent doping and paste process. The disadvantage of this process is that peak initiation can become more difficult due to the increase in planarity of the wafer.

The as-cut process requires that the 5-15µm saw damage is removed during the same time the peaks are formed. A single texturing process is used throughout with resulting peak heights being now 5-10µm. The advantages of this process are that only one chemical formulation is required and the larger peaks may assist with adhesion and contact formation for a given paste.

Figure 6 shows the relationship between reflectivity and amount of silicon etched per side (during texturing) for the as cut and saw damage removal processes mentioned above. The amount of silicon removed during the saw damage removal was 15µm. Reflectance drops substantially as the etching begins and plateaus sooner with the SDR approach. Ultimate reflectance values are slightly lower with the SDR method. The pictures show

the peak initiation and final peak height for both texturing conditions at corresponding stages of silicon removal. The smaller peak heights achieved with the SDR process condition are likely contributing to the slight improvement observed with reflectance. It is also interesting to note that for the as cut condition, the saw damage can be seen at the initial stages of peak formation as indicated by the arrows. The result of this evaluation indicate that the new additive can work well with both types of texturing processes and that reflectance is maintained over a wide range of silicon removal criteria.

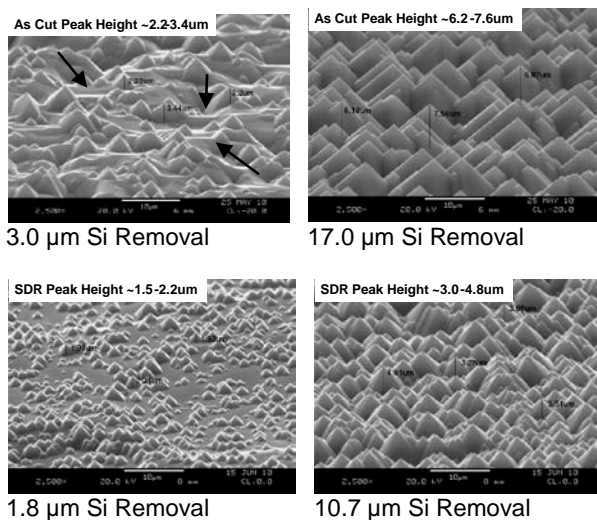
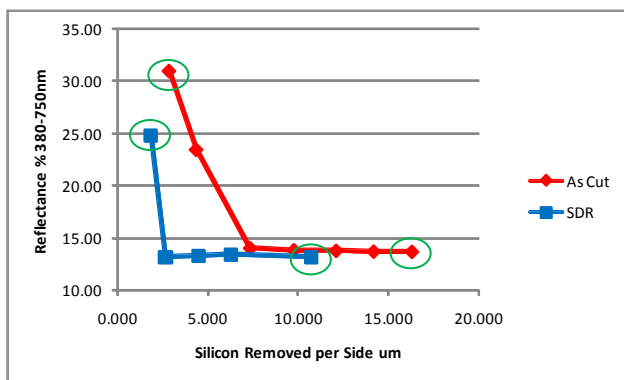


Figure 6: Evaluation of As Cut and SDR texturing with new additive

Environmental Impact

Due to more stringent waste water treatment regulations, it is important that any new material be compatible with established processes already in use. Biological Oxygen Demand (BOD) is often used to determine the level of oxygen consumed by organic waste in water while Chemical Oxygen Demand (COD) measures organic and any other species which may be contaminating the water. Total Organic Content measures the total amount of organics in solution. For all three responses, a lower

number represents a more environmentally friendly solution for a given measurement.

Table 2 below shows the relative environmental impact as defined by the measures mentioned above. The results show that the new additive process is compatible with existing IPA base texturing waste streams.

	IPA Process	New Additive
KOH g/L	40	60
IPA g/L	40	-
Additive g/L	-	4
BOD mg/L	130	Not Detected
COD mg/L	8700	1400
TOC ppm	3427	1125

Table 2: Environmental impact of the IPA Vs. the new additive

Performance Verification

Cell performance validation was evaluated independently at Fraunhofer ISE. Experiments were conducted to study the difference in cell performance using the new Dow additive compared to the standard IPA process used at ISE. Wafers were evaluated with and without the saw damage removal process previously described. Figure 7 below shows an overview of the process used and corresponding characterization points.

Process	Characterisation
Alkaline texturisation	Silicon removal, reflection
HF dip	
POCl ₃ batch diffusion	
PSG etch	Carrier life time
ARC (PECVD)	
Screen printing	
FFO	
LKI	IV sorter

Figure 7: Process flow used for cell performance verification

The table below summarizes the process conditions used for the evaluation. Wafers received no treatment after the cleaning process (as received) or had a saw damage removal step prior to texturing (SDR). The same texturing process conditions were used for the as received wafers and saw damaged etch wafers.

	IPA Process	New Additive
KOH g/L	10	60
IPA g/L	60	-
Additive g/L	-	5
Temperature °C	90	90
Dwell Time min	40	15

Table 3: Settings used during confirmation trial

Three different amounts of silicon removal were evaluated for reflectivity. Results are shown in figures 8 and 9.

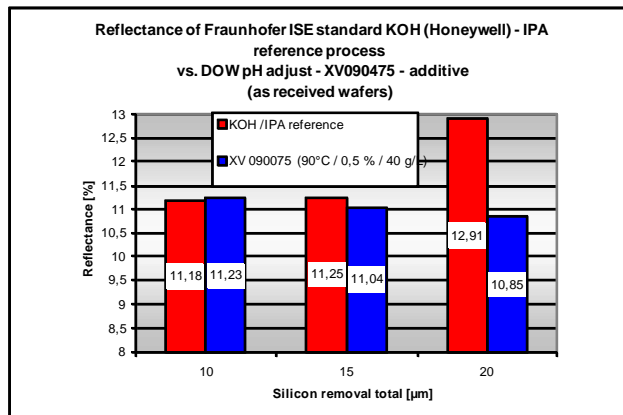


Figure 8: Reflectance vs. silicon removal for as received wafers (400-1100nm)

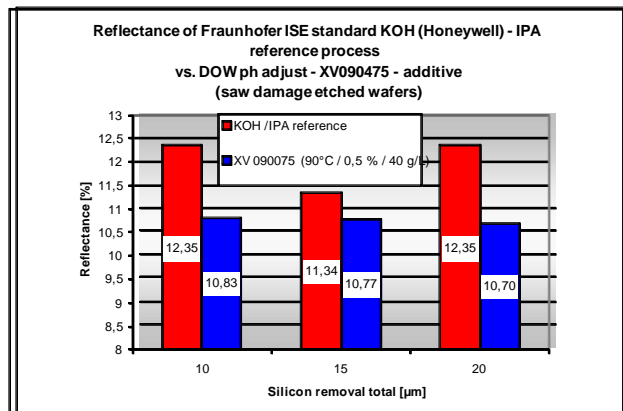


Figure 9: Reflectance vs. silicon removal for saw damaged etch wafers (400-1000nm)

The results reveal similar or better reflectivity values for all conditions evaluated. The results also suggest that the new additive process had less variability as compared to the IPA reference.

Wafers that received SDR and had a total of 20µm of silicon removed were processed through the end to finished solar cells. A summary of the results are presented in the tables below.

	ISE Ref	Additive
CE %	16.2	16.6
FF %	77.6	75.9
Isc mA/cm ²	35.6	36.1
Voc mV	602	607
Rseries ohm*cm ²	0.8	0.9
Carrier Lifetime µs	16.5	16.0

Table 4: Cell performance summary comparing ISE process to new additive for SDR wafers

Significant gains are observed for CE, Isc and Voc for the new additive and are most likely linked to the observed improvement in reflectivity. Rseries increased slightly which could explain the slight drop in fill factor. This could be due to non-optimized paste contact achieved with the different texturing processes. The slight difference in carrier lifetime is within experimental error.

In-line (horizontal) Texturing

Due to the volatility issues of IPA previously mentioned, mono-crystalline texturing is traditionally conducted in batch systems where the wafers sit vertically in wafer cassettes. These systems have process tanks that have less exposed surface area to the air thereby making it more compatible with the evaporative nature of the IPA. As-cut wafers were evaluated in an in-line texturing module similar in design to that used for multi-crystalline texturing. Process conditions used for the in-line evaluation are presented in Table 5.

	New Additive
KOH g/L	40
Additive g/L	6
Temperature °C	90
Dwell Time min	11

Table 5: Process conditions used during in-line evaluation of texturing additive

Results of the evaluation showed that it was possible to achieve reflectance values of approximately 11.5% as measured from 400nm-1100nm. Silicon removal was approximately 8µm per side for the 11 minute dwell time. The results as shown in figure 10 reveal satisfactory random pyramid formation with good uniformity and are similar to the results obtained in the vertical configurations.

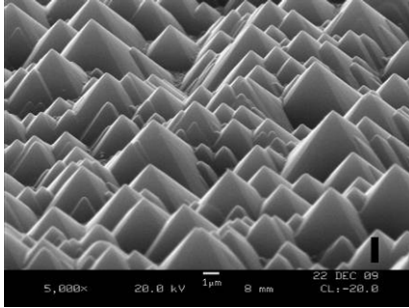


Figure 10: Typical texturing result obtained in horizontal texturing process

ACKNOWLEDGEMENT

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CONCLUSIONS

A new additive has been developed that enables IPA free texturing of mono-crystalline wafers. Results presented illustrate that the new additive is significantly more stable than IPA which allows for a much broader process window and will improve the overall cost of ownership of the process. Typical working bath dilutions of the additive exhibit similar or slightly improved performance as compared to the IPA based process. Results also indicated that the additive is compatible with as cut and saw damage removed wafers and that a wide range of peak heights can be achieved. Confirmation trials conducted at Fraunhofer ISE and results verified improved reflectivity performance vs. a control IPA process which translated into improved cell performance. Evaluations conducted on in-line texturing equipment showed similar reflectance and peak uniformity as typically achieved with more traditional vertical equipment configurations.

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