Investigation of Biodegradable Texturing Chemistries for Crystalline Si

Mark George[1], David Bohling[1], Helmuth Treichel[1], Avery Goldstein[1], Werner Kern[2], BG. Potter Jr.[3]
[1]Sunsonix™, 859 Pheland Ct, Milpitas, CA 95035, USA
[2]Werner Kern Associates, 22 Greenways Ln, Lakewood, NJ 08701, USA
[3] University of Arizona, Arizona Materials Laboratory, 4715 East Fort Lowell Road, Tucson, AZ 85712, USA
Mark George, phone: + (520) 822-6289, e-mail: mark@sunsonix.com

ABSTRACT: The cost of chemical waste disposal is high and the PV industry is discovering ways to eliminate harmful waste and its associated costs. In this paper we report on the results of exploring biodegradable chemistries that are useful for texturing c-Si substrates. We have found the role of additives to the texturing c-Si texturing chemistry to be three-fold. First the addition of additives stabilizes bath chemistry increasing the number of wafers processed in each bath turn, while at the same time decreasing reflectivity by providing more homogenous generation of texturing features. Finally these additives are now formulated to sequester efficiency-robbing transition metals like iron, chrome, nickel and copper that when present on a silicon wafer surface adversely influence the efficiency of the resulting PV devices. The additives come at a relatively high cost and while used in small quantities can be quite toxic to waste water streams. In the course of this investigation we were able to distinguish the efficiency improvement of the sequestering function and improved texturing function of several texturing additives. The efficiency gain by improved light trapping from texturing on nominally 18% efficient c-Si solar cells was determined to be about 0.4 % absolute. The removal of the transition metals offers another 0.15 to 0.25% efficiency improvement, but that gain comes from the use of fully biodegradable and non-toxic systems.

Keywords: c-Si, Etching, Solar Cell Efficiencies

1. INTRODUCTION

Alkaline etchants, such as NaOH and KOH, are routinely used in the processing of monocrystalline (100) solar cells, leading to the formation of pyramidal etch structures on the wafer surface. The high anisotropy of the etch solution exposes slow etching {111} faces, which intersect to form four-sided pyramids with facets at 54.7° to the wafer surface. These structures are well known to promote reflection reduction through multiple reflections of incidence of light and improved light trapping due to the oblique passage of light into the silicon surface.

The role of additives to the alkaline etchant such as IPA and state of the art additives is to improve the bath life of the etch solution and improve cell efficiency through optimization of light absorption and removal of metallic contamination.

Unfortunately the additives currently in use pose environmental and safety risks. For instance IPA not only is quite flammable but also exhibits some toxicity at high concentrations to aquatic species. It does however biodegrade over time. The bigger problem is in using IPA near its boiling point, can cause a significant fire hazard and unstable bath concentrations over time. Many alternative texturing additives on the market are more toxic than IPA, adding additional costs for remediation [1].

We have embarked on a project to develop a biodegradable additive that can eliminate or reduce the consumption of IPA and equal or exceed cell performance of currently applied non-biodegradable additives used to elevate cell efficiency.

2. EXPERIMENTAL

We have conducted trials with different commercial additives and several biodegradable candidate chemicals to determine their role in improving cell efficiency. A comparison to a standard KOH / IPA sequence for reflectivity, homogeneity, chemical residue and efficiency was made. In this sequence wafers were pre-cleaned in a DIW bath and then subjected to nominally 3 wt% KOH and 6 wt% IPA 20 minute etch at 80° C. The etch is followed by a DIW rinse and an HF/HCl neutralization bath followed by a DIW rinse and a HOT DIW pull. A second experiment was repeated with a texturing additive added to the KOH/IPA chemistry and a third experiment repeated where SX-E chemistry was added to the KOH/IPA bath [2].

This trial permitted us to ascertain the influence of each of the performance improvements by the texturing additive. Cell responses measured included average absolute non-solar weighted reflectivity (350 nm to 950 nm), FF, Jsc, Voc and absolute efficiency. SEM analysis of the etched silicon was also used as a benchmark for evaluation of biodegradable additives.

With this baseline performance documented we began our search for biodegradable additives using this data as a benchmark.

In subsequent experiments additives were added to KOH etchants with and without IPA. The concentrations of the additives was recorded and the response of etch rate (measured by weight loss), reflectivity, surface morphology measured by SEM and surface contamination measured by surface enhanced Raman spectroscopy are reported. Raman analysis was performed at an excitation wavelength of 532 nm. Certain experiments were selected for surface analysis of metallic components by SIMS (Secondary Ionization Mass Spectroscopy). Reflectivity was measured by use of a Xenon lamp for illumination with reflected light from the surface of the wafer collected by a 50 mm integrating sphere. The reflected light spectrum was measured by an Ocean Optics USB2000 spectrometer with a spectral range of 350 to 1000 nm. All samples were referenced to a NIST traceable Spectralon® diffuse reflectance standard.

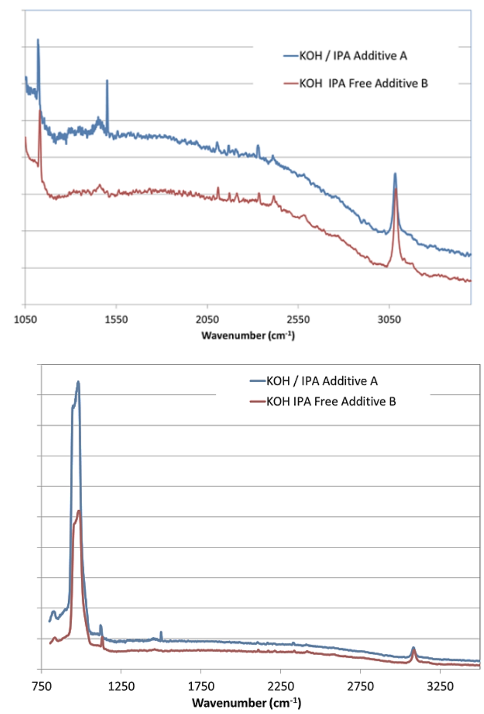
3. Distinction of Mechanisms for Efficiency Improvement By Texturing Additives

The sequestration of trace metals by SX-E from the chemical baths utilized to etch and clean crystalline Si wafers improves cell efficiency by between 0.15% and 0.3% absolute [2, 3]. In our previous work we focused on prevention of precipitation of metals from the chemical baths post texturing. In this present work we investigated the addition of the known metal sequestering agent, SX-E, into the alkaline texturing bath. In this study we wanted to separate the efficiency contribution of metal removal and texturing by commercially available additive, ***A***. It is readily observed that the commercial non-biodegradable additive both aids in reflectivity, decreasing the reflectivity by about 2.5% which accounts for about 0.39% absolute efficiency improvement for the measured cells. The balance of the improvement is garnered from removal of metallic contamination (0.18%).

Table I. Baseline Texturing Experiments

Texturing Chemistry	R_{avg} (%) 350 – 950 nm	Δ Eff(%)	Comment
KOH / IPA	12.8%	-	Baseline Process
KOH / IPA with Sunsonix SX-E	12.8%	0.18%	Baseline Plus Metal Removal
KOH / IPA Free with Sunsonix Additive 5	10.5%	0.38%	Sunsonix SF-X™

Upon conducting this experiment it was observed that there was an obvious surface wetting anomaly as the wafers from the IPA/KOH with additive ***A*** were pulled from the final HOT DIW bath. A representative wafer was analyzed and found to contain several peaks associated with organic functional groups which we attribute to a residue formed on the wafer surface that was not present with either the straight IPA or the IPA with SX-E. A representative survey spectrum of the observed Raman Shift is provided in Figure 1a and an expanded area showing multiple functional groups is shown in Figure 1b.



Figures 1a and 1b. Raman Survey Spectra of texturing additive A residue on textured wafer prior to emitter diffusion.

In further experiments we observed that other commercial additives and some of the biodegradable additives investigated also left a residue on the processed wafer surface. The residues, being composed of organic compounds, appear to cleanly burn off in the $POCl_3$ diffusion furnace since there is no evidence for cell efficiency degradation.

SEM image of the textured surface by the additive ***A*** provides an example of the homogeneity of the pyramidal features and their distribution a shown in Figure 2.

4. RESULTS AND DISCUSSION

Search for a Biodegradable Texturing Additive

Hydroxyl Functional Groups

It is clear from our Raman data (Figure 1a &b) that there is a variety of functional groups exhibiting different hydroxyl containing functional groups. Our investigation turned to finding a biodegradable texturing additive that could meet or exceed the reflectivity improvement of the commercial additive ***A***; we turned toward the family of organic compounds with hydroxyl functional groups, like IPA, while at the same time exhibiting low toxicity and biodegradability.

The family of chemicals with appropriate functional groups were determined to have widely different impact on etch rate and texturing quality. One feature quickly observed was that of inhomogeneity of the silicon etch depending on the additives used. The inhomogeneity exhibited itself in the form of "leopard" spots on the etched wafer surface. We quickly ascertained that there was a correlation to the presence, distribution, and size of the leopard spots and the size of the hydrogen bubbles emanating from the etched silicon.

The first series of investigations studied those additives for the baseline KOH/IPA texturing chemistries. One of these additives (number 2) exhibited excellent total reflectivity, comparable with the commercial additive. In Figure 3 the evolution of the reflectivity as a function of etch time is presented. Some additives tend to slow the etch rate of the silicon while others enhance the etch rate. Additive 2 represents the best performing additive. This chemistry does require IPA, but unlike the commercial additive, ***A***, it is completely biodegradable. One of the added benefits of this chemistry is that the etch rate dramatically slows down at the 20 minute mark, providing for a very forgiving process.

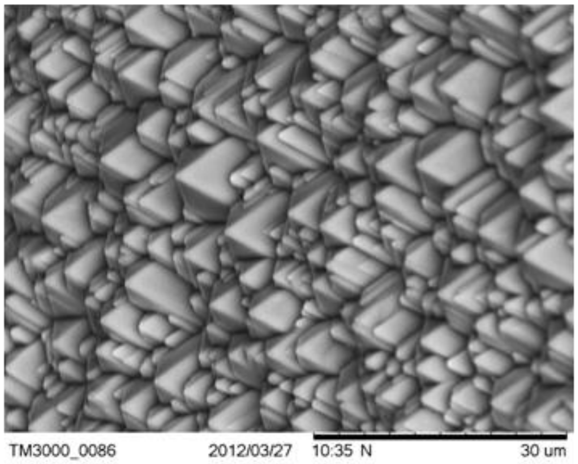


Figure 2. SEM of c-Si textured with additive A.

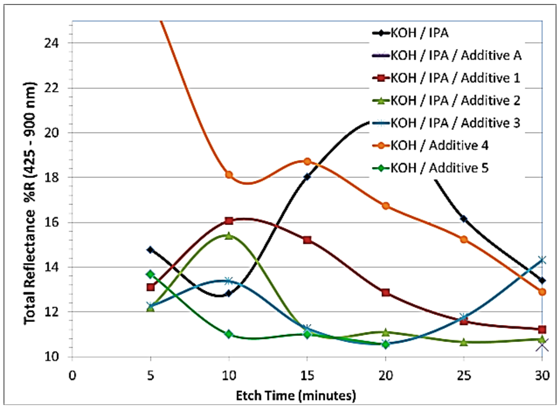


Figure 3. Reflectivity vs. etch time for different etch chemistries.

The etch rate for these experiments all tend to trend in the same way. Initially the etch rate is fast and then slows with time as the pyramidal features form. Several of the chemical additives almost completely quenched the etch rate and in others there was almost a complete loss of anisotropy, as shown in Figure 4.

The elimination of IPA as a constituent of the texturing bath is also very important for long bath life and to eliminate the concern for flammability since the bath temperatures are used for IPA are near the boiling point and above the flash point of IPA. We therefore turned our focus for elimination of IPA and instead towards those additives with boiling points above 200 °C.

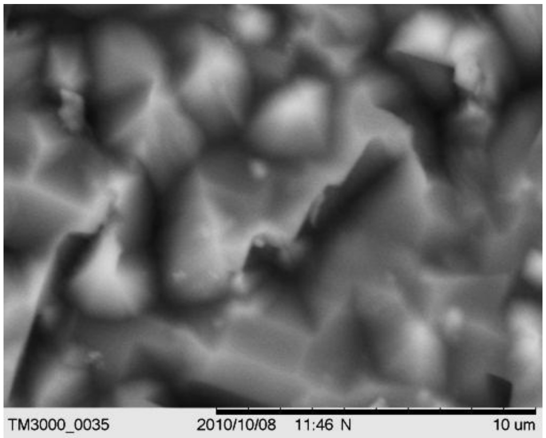


Figure 4. Loss of anisotropy by the use of biodegradable texturing additive 3.

Some of the IPA free additives exhibited inhomogeneous etch patterns, exhibiting pyramidal islands, such as those observed in Figure 5.

Finally the best performing biodegradable additive exhibits a classic homogenous texturing with uniform pyramidal structures such as those shown in Figure 6 and matches the average reflectivity of the commercial additive ***A*** with an average reflectance of 10.5%.

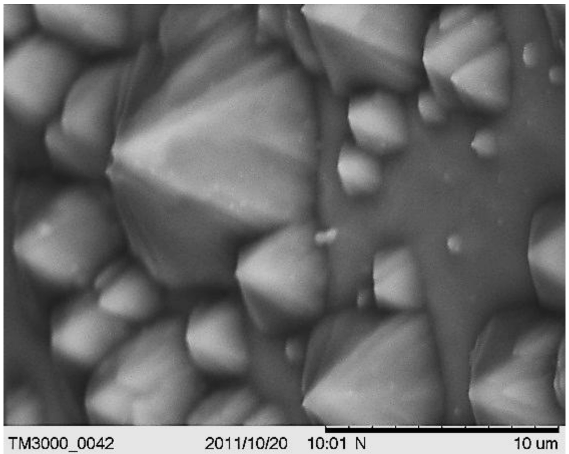


Figure 5. Inhomogeneous etch by biodegradable texturing additive 4.

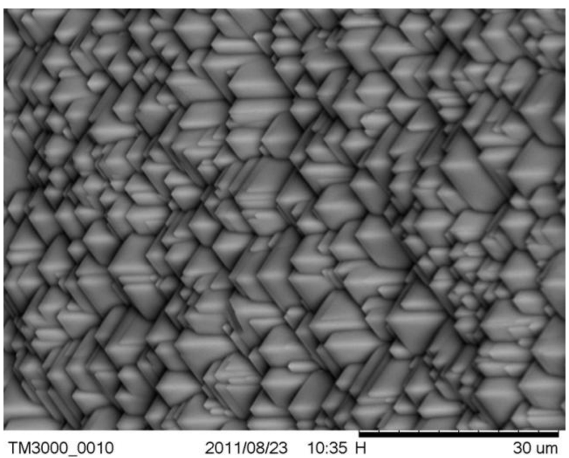


Figure 6. Best performing biodegradable texturing additive 5.

The IPA free texturing additive 5 not only matches the reflectivity of commercially available KOH/IPA texturing additive ***A***, it also eliminates metal surface contamination providing a total cell efficiency improvement of 0.56% absolute over the KOH/IPA baseline process.

5. Summary and Conclusions

The uses of additives for improving the texturing of silicon etch and removal of trace transition metals is now standard in the c-Si PV manufacturing process. However these additives are toxic to the environment and still rely on IPA to provide the best surface morphology. We have shown that a biodegradable chemistry can meet the performance of non-biodegradable additives and eliminate the use of IPA. Biodegradable additives are safe for the environment and enable the PV industry to further reduce its environmental impact.

ACKNOWLEDGEMENTS

The authors thank Dr. J.B. Kana- Kana for support on gathering the Raman Spectra. This project was supported by the US Department of Education; the Arizona Governor’s Office of Economic Recovery and the Arizona Research Institute for Solar Energy (AzRISE).

REFERENCES

[1] KOH/SURFACTANT AS AN ALTERNATIVE TO KOH/IPA FOR TEXTURISATION OF MONOCRYSTALLINE SILICON, Wefringhaus, A. Helfricht, International Solar Energy Research Center Konstanz, 24th EUPVSEC 2009, 2CV5.41

[2] Crystalline Silicon Solar cell Efficiency Improvement by Advanced Cleaning Technology, D. Bohling, H. Treichel, T. Lazerand, A. Goldstein, and M. George, Tech NSTI-Nanotech 2010, Vol. 3, 2010, pp. 704-707

[3] Removal of Trace Metals Using a Biodegradable Complexing Agent, H. Treichel, A. Goldstein, M. George, D. Bohling, J. Rentsch, A. Oltersdorf, M. Zimmer, S. Ostrowski, I. Mowat, L. Wang and W. Kern, Photovoltaics International Q2 2011, pp 81-93.