A HF-FREE CHEMISTRY ALTERNATIVE FOR MULTICRYSTALLINE WAFER TEXTURING

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ABSTRACT: The texturing step for multicrystalline photovoltaics, which reduces reflectance and improves efficiency of the cell, is a critical step in the ultimate performance of the cell. Current texturing technologies for multicrystalline silicon requires the use of large quantities of concentrated and hazardous chemicals. The handling, storage, use and disposal of these solutions requires extreme care and can be a significant expense depending on local and regional treatment requirements. To texture multicrystalline wafers, the photovoltaic (PV) industry currently uses concentrated hydrofluoric (HF) and nitric acid (an exothermic reaction) to a make a texturing bath[1]. The new technology presented is this paper focuses on a more dilute proprietary alkaline chemistry that is much lower in cost (material and waste treatment cost) and safer to handle. Unlike typical generic alkaline chemistries[2], this chemistry behaves more isotropically when exposed to the different crystal planes on a multicrystalline wafer. This proprietary alkaline chemistry delivers equivalent reflectance as the HF/nitric process while significantly reducing the health, safety, and environmental issues associated with the current technology. (Keywords: Cost Reduction, Multicrystalline Silicon, Texturisation).

1 BACKGROUND

The current texturing technology for multicrystalline silicon wafers involves the use of a corrosive and toxic combination of concentrated hydrofluoric (HF) and nitric acid. The hazards associated with HF[3] and nitric acid[4] are well documented. Beyond the safety and handling concerns, the HF/nitric process requires the use of high concentrations of both acids in order to achieve fast silicon etch rates and consistent etch performance across all crystal planes. Those high concentrations can have a significant impact on the overall cost of texturing multicrystalline wafers.

A substantial advantage, however, of the HF/nitric chemistry is the isotropic nature of the silicon etching process. Essentially, the concentrated nitric acid uniformly oxidizes across the various crystal planes while the fluorine in the HF reacts with the oxidized silicon to form water soluble silicon salts. The result is a very uniform texture without regard to the different crystal orientations and geometries present on the multicrystalline wafer surface.

One alternative to the HF/nitric chemistry would be the use of generic alkaline processes. With generic alkaline chemistry, the solubility of the various silicon crystal planes is significantly different. For example, the <100> crystal plane can etch 7.5 times faster in a 5% sodium hydroxide solution at 70C as compared to the <111> crystal plane. This anistropic etching behavior is a desirable feature when trying to form pyramids on a monocrystalline (mono) silicon wafer.[5] For mono wafers and with generic alkaline chemistry, the <100> crystal plans are etched quickly and <111> planes remain essentially unetched forming the pyramidal structure on the wafer. As a result of this anisotropic etching characteristic, alkaline chemistries are used almost exclusively for the texturing of monocrystalline wafers.

A unique challenge in the texturing of multicrystalline wafers is the exposure of the different crystal plans at opposing geometric orientations on the surface of the wafer. Because the <111> crystalline surface could be oriented essentially normal to the plane of the wafer, that crystalline plane could remain virtually untouched by the generic alkaline chemistry resulting in high and variable reflectance values.[6]

Another alternative to the HF/nitric chemistry for texturing multicrystalline solar cells is reactive ion etching (REI). Using this isotropic plasma technique, a uniform and non reflective surface can be created on the wafer surface.[7] However, the REI process is quite costly to run and surface defects created during processing can become problematic.

2 EXPERIMENTAL OBJECTIVES

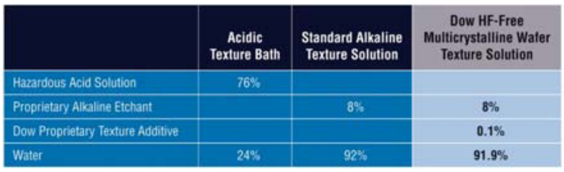
Given the above mentioned obstacles and challenges, the following objectives were set for this project:

- Replace traditional acidic texturing solutions with proprietary alkaline chemistry;
- Improve process safety;
- Reduce operating cost by decreasing chemical demand and significantly reducing the waste management costs;
- Produce a textured surface with similar or improved reflectance value as compared to the standard HF/nitric process while maintaining cell efficiency.

3 PROCESS COMPARISONS

For this project, three different chemistry types and processes were compared. They included the HF/nitric control process, a generic alkaline chemistry and a developmental alternative process. The recipes for each of the three chemistries are described in Table 1.

Table I: Texture Chemistry Comparisons



	Acidic Texture Bath	Standard Alkaline Texture Solution	Dow HF-Free Multicrystalline Wafer Texture Solution
Hazardous Acid Solution	76%		
Proprietary Alkaline Etchant		8%	8%
Dow Proprietary Texture Additive			0.1%
Water	24%	92%	91.9%

One key observation from Table I is that the two alkaline processes require significantly less chemistry when making up the working bath. For Dow's proprietary version, only 8.1% of the bath is active chemistry (Figure 1).

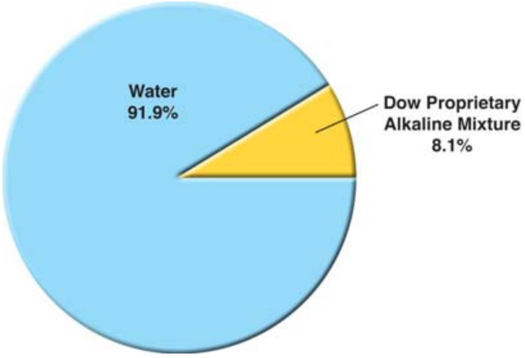


Figure 1 – Dow Developmental Alkaline Chemistry Recipe

For HF/nitric, 76% of the bath is active (Figure 2).

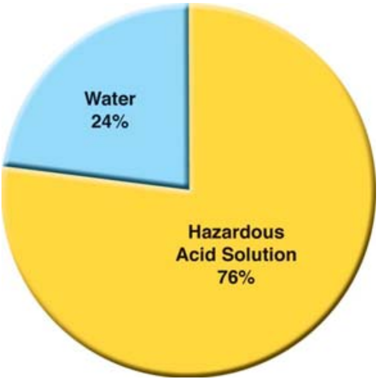


Figure 2 – NF/Nitric Control Recipe

With almost ten times less chemistry used for make-up, the potential cost savings is obvious. In addition to the working bath savings, the amount of hazardous waste that needs to be treated for the developmental alkaline process also drops by approximately ten times.

When examining the potential for reduced cost, it is also informative to review the reaction stoichiometry of both the alkaline and acid processes. In Figure 3, the HF/nitric reaction involves the consumption of six moles of HF for every mole of silicon dissolved in the form of hexafluorosililic acid.

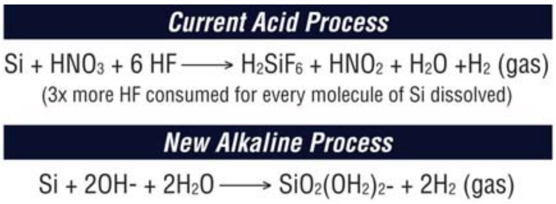


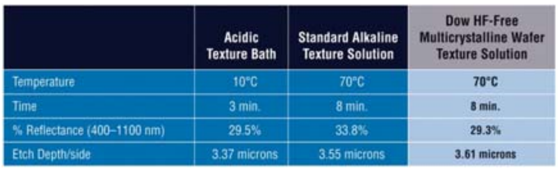
Figure 3 – Stoichometry Comparison – Acid versus Proprietary Alkaline

In the case of the new alkaline process, only 2 moles of hydroxide is consumed for everyone mole of silicon dissolved in the form of silicate salt. That would represent a 3x reduction in the consumption of chemistry.

Getting to a lower cost model for the developmental chemistry was not particularly challenging because of the high costs associated with the standard HF/nitric process. The most significant technical challenge was to overcome the inherent, anisotropic nature of the alkaline chemistry to allow for a uniform texture and low reflectance.

In Table II, the three different texturing processes and the initial results are compared.

Table II: Texture Process Comparison



	Acidic Texture Bath	Standard Alkaline Texture Solution	Dow HF-Free Multicrystalline Wafer Texture Solution
Temperature	10°C	70°C	**70°C**
Time	3 min.	8 min.	**8 min.**
% Reflectance (400–1100 nm)	29.5%	33.8%	**29.3%**
Etch Depth/side	3.37 microns	3.55 microns	**3.61 microns**

For HF/nitric, the process temperature is 10^{o}C and the standard dwell time is about 3 minutes. The lower temperature is required to help control the strongly exothermic reaction of the HF/nitric with the silicon on the wafer surface. After three minutes, approximately 3.4 microns of silicon per side is removed. That represents an etch rate of about 1 micron of silicon per minute. For this experiment, a target range of 3 to 4 microns of silicon removal per side was targeted. The overall performance of the three chemistries are compared at equivalent amounts of silicon removal.

As shown in Table II, the generic alkaline and developmental Dow process had to be run at higher temperature (70^{o}C) and for a longer dwell time (8 minutes) in order to achieve the same level of silicon removal for this comparison. It should be noted that in the case of Dow's developmental chemistry, a faster etch could potentially be achieved with higher chemistry concentrations and/or higher temperatures.

At the equivalent etch amounts, the reflectance of the HF/nitric process is very similar to the Dow's proprietary process (see Figure 4)

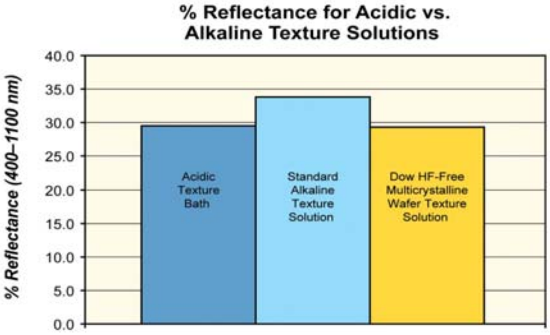


Figure 4 – Reflectance Comparison

For the generic alkaline process, the reflectance at the equivalent etch depth are higher than both the acid control and the developmental product. One potential cause of the higher reflectance is the previously mentioned anisotropic etching behavior of the generic alkaline chemistry.

As illustrated in Figure 5, the generic alkaline chemistry does not etch each of the crystal planes evenly. The SEM image on the left in Figure 5 shows significant crystal grain boundary delineation as compared to Dow's developmental process in the SEM image on the right.

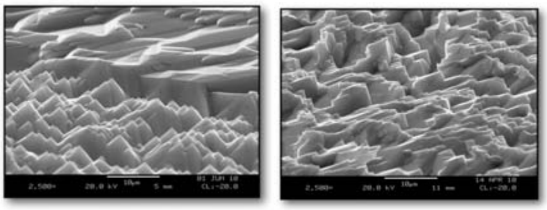


Figure 5 – SEM's of Textured Surfaces (Generic Alkaline – Left; Dow Proprietary Alkaline – Right)

Along with the higher reflectance and poor uniformity, this grain boundary delineation can also contribute to poor electrical performance because of the potential for surface recombination and carrier lifetime issues.[8]

When comparing the Dow process to the HF/nitric control process (see Figure 6), the surface with the proprietary alkaline process shows an improved degree of isotropic behavior.

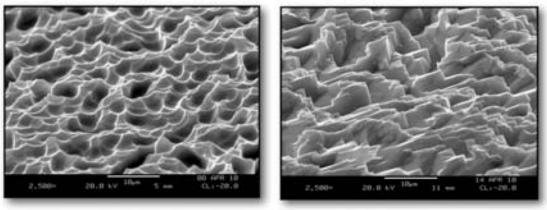


Figure 6 – SEM's of Textured Surfaces (HF/Nitric – Left; Dow Proprietary Alkaline – Right)

Even though the surface is more uniform with the Dow alkaline process, the surface roughness is still quite different (see Figure 6). At this point, it has not been determined whether that observed difference will have a positive or negative impact when it comes to carrier lifetime, silicon nitride deposition and other basic cell properties.

4 CONCLUSIONS

It has been determined that a proprietary alkaline blend of chemistries can be found that behaves more isotropically than generic alkaline chemistries used alone. This developmental chemistry can produce similar reflectance to the HF/nitric control process at a fraction of the cost. In addition, this new process has significantly less environmental impact by using less chemistry and materials that are inherently less toxic.

5 FUTURE WORK

Even though the cost reduction potential and general performance is quite encouraging, this project is still considered to be developmental. In particular, the effect of the different surface structures created with the Dow Texture Process on cell electrical properties still requires further investigation. Dow is currently working with a Photovoltaic Institute to verify the electrical properties that could be influenced by the changes to the surface texture illustrated in figures 5 and 6. At this point, it is obvious that the surface has a different roughness and appearance; however, it is unknown whether that difference in surface structure will be a positive or negative influence as it relates to carrier lifetime, silicon nitride coverage, surface passivation, and cell efficiency.

Additional formulation efforts are on-going to further optimize the basic performance of the alkaline texturing chemistry. In particular, the uniformity across crystal plans and the overall etch rate are receiving focused attention.

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