Wafer Cleaning and its Effects on Subsequent Texturing Processes

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Abstract

Interfacial surface phenomenon and treatments has been exhaustively explored for the semiconductor industry for advanced material surface preparation. The RCA clean process is a standard for the IC industry[1]. Unfortunately, the needs for the photovoltaic (PV) industry are different in scope and purpose. Exploring the topic of surface cleaning and how different chemistries influence downstream processing like texturing and metallization, it is hoped that attention can be drawn to some of the critical process interactions unique to the PV industry.

1.0 Introduction

In the production of mono and multi crystalline solar cells, a number of processing steps are required. Some of the most prominent steps are outlined in Table 1.

Table 1 – Manufacturing Steps – Crystalline Cells

Process Step	Process Description
1	Ingot Sawing/Wafering[2]
2	Glue Removal and Final Clean
3	Texturing
4	Emitter Doping
5	SiNx Deposition
6	Metallization
7	Cell Characterization

A great deal of focus has been directed to optimizing each of the individual process areas. However, until recently, limited investigations have been made exploring the interactions and interdependence of one processing step to other subsequent steps. For example, how does the choice of cleaner influence the types of structures formed after texturing? How does the type of texture and peak density influence metal adhesion? By not focusing on all the nested interactions, complete process optimization becomes difficult if not impossible.

Some of the key interactions that require attention are the following:

(1) the interaction of cutting fluids and slurries with cleaning chemistries
(2) the interaction of cleaning chemistry on texturing
(3) the influence of texture on doping and SiNx deposition
(4) The effect of texture type and peak density on ink or metal adhesion.

For this paper, the interaction of wafer cleaning and texturing will be explored in detail. It has been determined that the type of chemistry used in the cleaning process has a profound influence on the quality and reproducibility of the final texturing.

2.0 Typical PV Industry Cleaning and Texturing Practices

After wire saw, glue removal and wafer singulation, a final clean is done on the wafers. The purpose of the final clean is to remove all slurry, cutting fluid and wire saw residues from the wafer surface. Typically, this residue consists of varying amounts of PEG or mineral oil (cutting fluids), iron and copper oxides, silicon carbide, and ground silicon. These residues can be literally burnt onto the wafer surface by the heat of friction introduced during the sawing process. To remove this residue, the correct chemistry needs to be chosen that will complement the equipment that is used. For automated cleaning lines, both horizontal and vertical cleaning machines are available commercially. Both of the systems are capable of processing wafers at elevated temperatures and both typically have ultrasonic cleaning capability. As cleaners are designed for this purpose, care must be taken to make sure they are optimized to work when exposed to the cavitation introduced with ultrasonics[3]. Targets are a uniform appearance, low metals (determined by extraction and atomic absorption analysis) and no black (metals) or white spots (over etch). A variety of cleaners are available commercially (including Dow's proprietary Enlight 320 and 340 series of cleaners[4]) that operate successfully with the above described equipment and cleaning criteria. These cleaners are available in neutral, acidic or alkaline pH's. Recently, it has been determined that beyond the quality of the clean (uniform, no metals), the type of chemistry chosen for cleaning can have a profound influence on the subsequent texturing step.

3.0 The Influence of Different Cleaning Chemistries on Subsequent Texturing

After wafer cleaning and given a sufficient amount of time for a native oxide layer to develop, monocrystalline Si wafers will exhibit a hydrophilic surface having a contact angle of 0°. If these wafers are then subjected to a typical alkaline texturing process (e.g. KOH with moderating solvent at 90C), pyramids will nucleate to a preferred density and grow to heights between 5-8μ.m, minimizing percent reflectance. An optimally textured wafer (figure 1) will be classified by its uniform pyramid height and distribution and a reflectance of < 14% (360-750nm range).

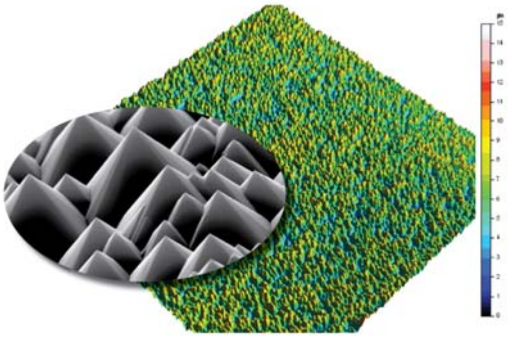


Figure 1 – SEM and Surface Profile Optimally Textured Surface

The importance of the wafer surface state is seen when texturing immediately follows an alkaline cleaning process, resulting in non-uniform pyramid nucleation and a reflectance of > 20% (see Figure 2). A typical alkaline cleaning process (e.g. KOH and cleaning chemistries at 50C) will remove the native oxide from the wafer, as evidenced by weight loss analysis and the resulting hydrophobic nature of the surface.

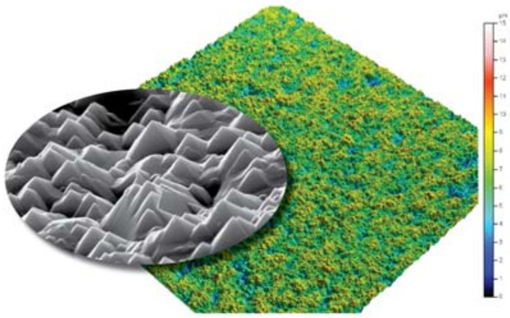


Figure 2 – SEM and Surface Profile of Alkaline pH Cleaner after Texturing

Contact angle increases from 0° to > 50° (figure 7). Texturing etch depth also decreases following alkaline cleaning, from 8μ/side to 3μ/side (figure 6). This is due to the increased exposure of the (111) crystallographic planes on the non-optimally textured wafer surface. Light trapping is not as successful on the randomized surface, which may lead to decreased cell efficiencies down line.

Other cleaners, including acidic and pH neutral solutions, were evaluated prior to the texturing step. Acid based cleaners are known to have the capability to remove metals from the surface without etching the silicon surface. Since metals are known to influence the etching rate of silicon[5], it was expected that the etch rate should change with use of the acid cleaner. For this experiment, Dow's WaferClean 324 was used to clean the wafer prior to texturing. After cleaning, the wafer contact angle was unchanged , remaining at 0° (figure 7). After texturing, an increase in the texturing rate was observed (due to the metal reduction) and reflectance was comparable to the neutral control (figure 6). The peak height and density was also very similar to the control with slightly larger peak heights (figure 3).

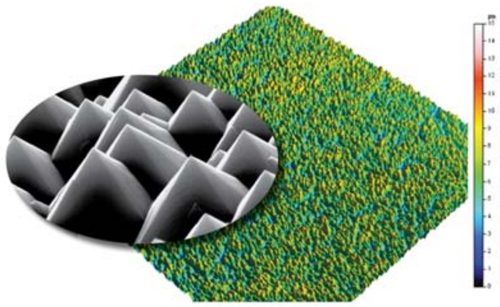


Figure 3 – SEM and Surface Profile of Acid pH Cleaner after Texturing

4.0 HF Effects and Reversibility

A known oxide removal step involving Hydrofluoric acid exposure also demonstrated the importance of the silicon surface state prior to entering downstream processing steps, notably wafer texturing. Wafer contact angle increased from 0° to 69° following an HF acid dwell. Alkaline texturing immediately following this exposure (figure 4) resulted in a high density of pyramid nucleation points, demonstrating low etch loss (< 4μ/side) and increased reflectance (> 14%).

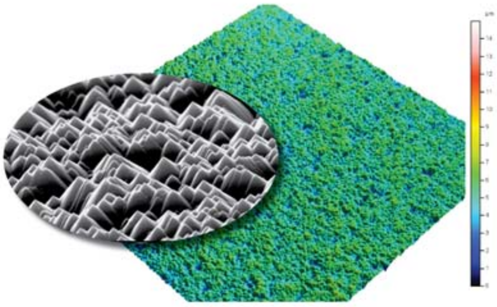


Figure 4 – SEM and Surface Profile of HF Exposure Prior to Texturing

Etch loss was again inhibited by the increased evolution of exposed (111) crystallographic planes.

Understanding that removal of the native oxide layer without allowing adequate time for re-growth negatively impacts texturing, there is the opportunity to accelerate oxide growth to achieve optimal texturing. Following alkaline cleaning, wafer contact angle increases to > 50°. If the wafer is then subjected to a proprietary re-oxidation step, contact angle returns to zero and texturing returns to a preferred state (figure 5).

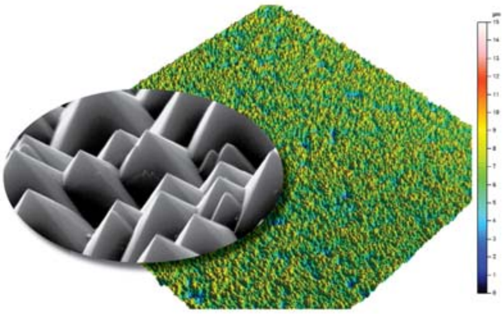


Figure 5 – SEM and Surface Profile of Alkaline Clean Followed by Re-Optimizing with a Proprietary Clean Followed by Texturing

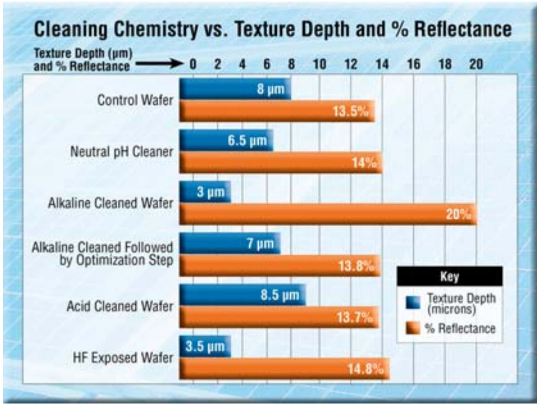
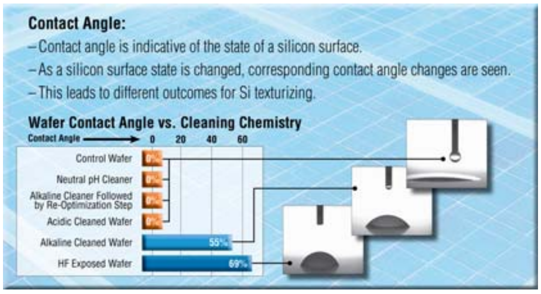


Figure 6- Contract Angle vs. Cleaning Chemistry



Contact Angle:

– Contact angle is indicative of the state of a silicon surface.

– As a silicon surface state is changed, corresponding contact angle changes are seen.

– This leads to different outcomes for Si texturizing.

Figure 7 – Cleaning Chemistry vs. Texture Depth and Percent Reflectance

5.0 Conclusion

Wafer cleaning can have a profound effect on the surface state of Si wafers and texturing results; particularly when that cleaning disturbs the native oxide layer of the wafer. Alkaline cleaners, which etch through the native oxide layer, produce poor results when immediately followed by a texturing step. Decreased etch amounts and increased percent reflectance are observed. Hydrofluoric acid similarly removes the native oxide layer, also producing poor texturing results as a consequence. Further work has shown this to be a reversible occurrence as a re-oxidizing step can restore the native oxide and texturing returns to an optimal level. Alternative cleaners, including acidic and pH neutral products, do not disturb the native oxide layer and thus do not impact the subsequent texturing step. It has been shown in this paper that wafer processing steps do not occur entirely independent of each other, but rather demonstrate interactions that can negatively impact cell construction. If these interactions are understood, they can be avoided or corrected to produce an optimally efficient photovoltaic cell.

6.0 Acknowledgments

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7.0 References

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