How to overcome the effects of silicon build-up during solar cell wet chemical processing

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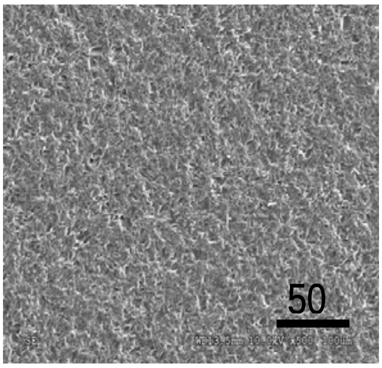
Introduction

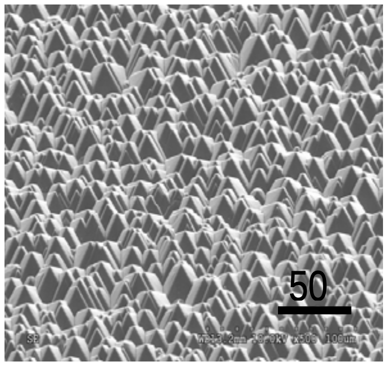
Although the chemical reaction is well known, the anisotropic etching of Si in alkaline solutions is a complex process. This is particularly true in the solar industry where a large mass of silicon is typically introduced into the etch bath. The etch by-products (silicates) affect the balance of the etching specie. If adequate compensation is not made for these by-products, a significant drop in etch rate and an increase in contamination levels is typically noticed. Because of this contamination, production lines would suffer from unpredictable wafer characteristics and hence lower cell performance.

In order to obtain stable and reproducible manufacturing processes, a reliable and accurate real-time measurement of the etching constituents becomes necessary. In addition, a mechanism by which fresh chemicals can be added to the etching bath is also required. The presence of these etch by-products has been shown to slow down the etch rate even when the chemical concentration is correct. Simply put, the solubility of etch by-products decreases once the concentration of silicates increases. And hence, Si mass transport from wafer surface to the etching solution is impacted. Chemical mixtures involved in solar cell manufacturing generally include: KOH/IPA, HF/HNO_3, HF/HCl, and other compounds. Additives, e.g. surfactants, are typically used to enhance etch uniformity.

In this study, wafers were processed in a KOH/IPA mixture to produce texturized surfaces as shown in Figure 1. In-line sensors were installed to monitor the chemicals' concentrations in real-time. Algorithms were developed to control the chemical concentration by injecting chemicals and water at a desired time interval to compensate for the loss of chemicals and water. The system also allows for draining and replenishing the chemicals and water to keep the silicates under a threshold to maintain consistent etching characteristics under different bath loading conditions.



As-cut Surface



Fully Textured Surface

Figure 1: A Sample of surface texturization
at 2% wt KOH and 4% wt IPA at 80°C

Experimental

Wet chemical processes were conducted on a fully-automated GAMASolar™ wafer etching and cleaning station. The batch size was 200 wafers per run. All tests were performed with the same wafer supplier, including wafers from about 100 different ingots. Silicon etching processes were conducted with the aid of Akrion Systems' patented in-situ chemical concentration control system (ICE-1™). Measurements of concentrations were taken using inline NIR (near infrared) sensors installed in the recirculation loop of the process tanks. These sensors measure light absorbance and transmit it through fiber optics cables to an array of detectors (spectrophotometer).

The light absorbance of given specie in the solution is correlated to its concentration over a wide range of wavelengths. The signal is then reported to an amplifier that scales the response to a 4-20 mA output. This signal is subsequently fed into an analog module that scales the signal and reports directly to the system computer which controls the spiking (volumes and frequency) of chemicals to maintain concentration. A variety of chemicals e.g. HF, HNO_3, HAc and applications were also studied but only the results of KOH/IPA control will be presented here. The goal was to produce consistent etch rates and texturization patterns similar to those shown in Figure 1 over the entire bath life and different silicon loading levels.

Results and Discussion:

This technology provides technical advantages by accurately measuring the concentration of chemicals to produce the desired process results – in this case the texturization pattern [1-3]. Controlling concentration for uniform, repeatable texturization will help solar cell manufacturers reduce cost of ownership (COO) and overall cost of manufacturing by extending the usable life of the chemical bath, which in turn extends the up-time and overall utilization of the tool [4-5].

Figure 2 shows the calibration curve of the concentration of KOH. Similar calibration is typically run for IPA. Figure 3 shows the amount of KOH that is required to maintain a stable etch rate over time. As can be seen from Figure 3, the volume of KOH required for maintaining a constant etch rate (ER) is linearly related to the mass of Si being etched. The data is in excellent agreement with stoichiometry and stands good grounds for production applications. The system is also calibrated to track the etch byproducts (measured as Si) as shown in Figure 4.

Results have shown that the dissolved Si in the bath must be maintained below a threshold limit. Akrion Systems has implemented an algorithm to control Si concentration in the bath as well, so the etch rate is maintained. This algorithm allows the capability to spike known volumes of fresh chemicals and drain out old chemicals. The system is therefore able to maintain the concentrations of chemicals as well as the etch by-products. As a result, consistent wafer processing as shown in figures 5 and 6 for reflectance and Si etch rate, respectively, is achieved. Unstable etch rate was shown before in the case of no ICE control as can be seen from figure 7. Longer utilization of the bath and lower cost of ownership is easily attained.

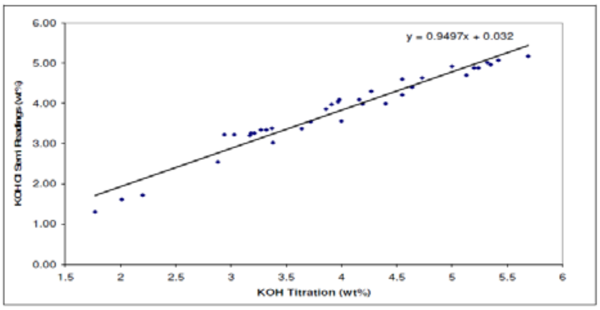


Figure 2: Measured and predicted concentrations of KOH.

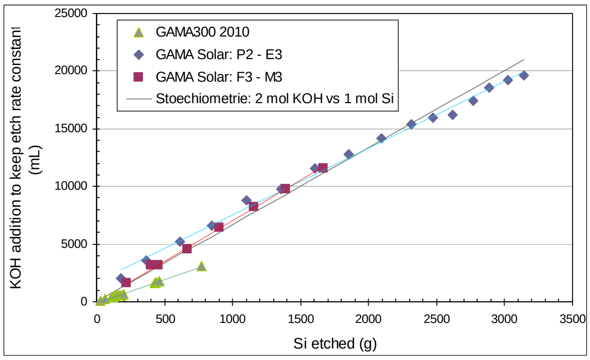


Figure 3: Volumes of KOH required to etch Si in production is in agreement with theory.

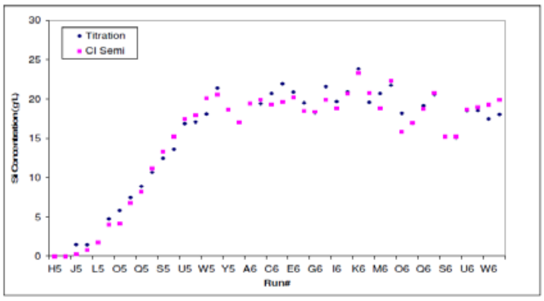


Figure 4: Concentration of dissolved Si under real time processing.

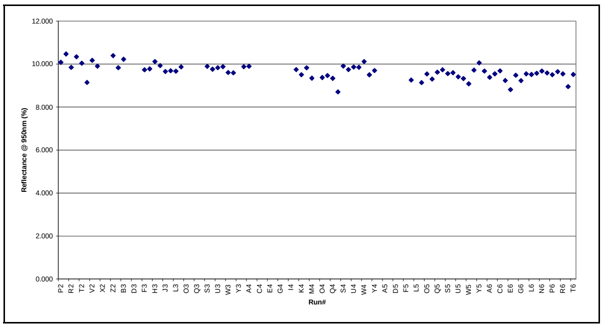


Figure 5: Reflectance of texturized wafers vs. multiple process lots.

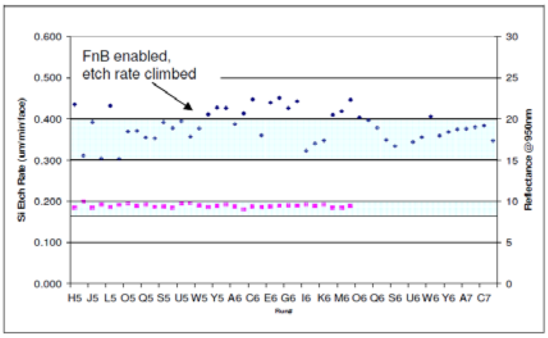


Figure 6: Etch rate (ER) and reflectance over time with dynamic feed/bleed and ICE controls.

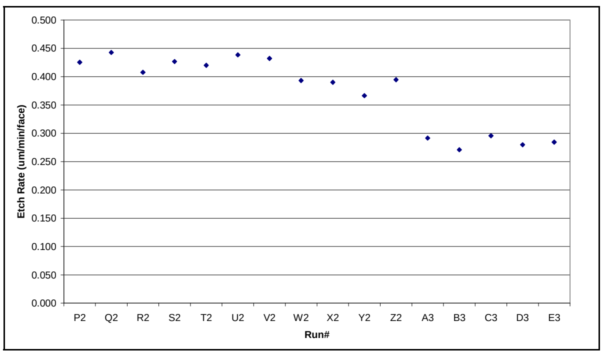


Figure 7: Etch rate (ER) over time without dynamic feed/bleed and ICE controls.

Conclusions:

Results show that real-time chemical concentration monitoring and control are critical and beneficial for advanced solar cell manufacturing. The technology reduces the days required for field installation by eliminating the time and resources required to dial-in the right chemicals' concentrations. Utilizing closed loop concentration control, this process will no longer require many iterations and tedious work until the results are achieved. The technology significantly reduces rework and wafer miss-processing and hence the manufacturing becomes more robust and less costly.

References

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