CORRELATION BETWEEN CONDUCTIVITY AND PH MEASUREMENTS FOR KOH TEXTURING SOLUTIONS AND ADDITIVES

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ABSTRACT: The ability to control the chemical concentration of etching baths is a critical step in being able to achieve uniform and repeatable texturization of solar cells. It also maximizes the chemical usage by being able to extend the usable bath life of the process. This in turn, cuts down on waste and reduces the overall cost of ownership (COO). The use of conductivity as a means of control has long been in use for oxide etching baths. The ability to extend that technology to other chemicals has been explored. This paper demonstrates the use of pH and conductivity sensors to monitor and control the concentration of KOH solutions. The effects of various additives as well as silicate buildup on pH and conductivity have been investigated and the results showed that the bath life can be extended and stable processes obtained.

Key words: solar cells, texturization, silicate, IPA-free, conductivity, pH

1. INTRODUCTION

Global demand for photovoltaic energy has reached more than 30GW and is still growing. This rapid growth is primarily due to the radical reduction in the price of various components of the value chain, including manufacturing steps [1-5]. In order to obtain stable and reproducible manufacturing processes, a reliable and accurate real-time measurement of the etching constituents becomes necessary [1-3]. The chemical mixtures of interest in the photovoltaic industry include KOH/IPA and/or KOH/IPA-free additives. While standard analytical techniques (e.g. NIR, UV spectroscopy) are sometimes used for concentration monitoring, conductivity cells and pH electrodes can provide fast and very cost-effective real-time control for such baths.

The industry has routinely used conductivity as a concentration control method for such chemicals as HF and HCl. Any mixture that can transmit electricity or heat is considered conductive. Therefore, a mixture such as an acid or base, which dissociates in solution will conduct electricity due to the dissolved ions in solution. The degree of dissociation as well as the bath concentration determines the overall conductivity of the mixture. Strong acids and bases dissociate completely and, therefore, have higher conductivities than weak acids and bases that only partially dissociate in water.

The etchants used in the photovoltaic industry (e.g. KOH, NaOH) dissociate in water, therefore, the conductance of these solutions can be measured and monitored during the etching process. Figure 1 shows the conductivity of several acids and bases versus concentration. It can be seen that the conductivity increases with increasing concentration until it reaches a maximum.

When a solution becomes sufficiently concentrated, the degree of dissociation slows down. Any further increase in concentration results in the interaction of the ions in solution, which causes a decrease in the conductivity. It should be noted, however, that the concentrations used in the photovoltaic industry do not reach this maximum, therefore, conductivity can be used

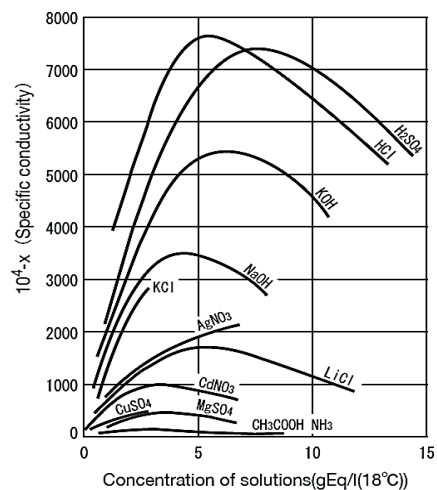to detect chemical concentrations in a fairly accurate manner.

Figure 1: Conductivity vs. Concentration for various solutions

The dissociation of acids and bases also lends itself to measuring the pH of a solution. By considering the hydrogen ion (H^+) concentration, the pH of an aqueous solution can be measured. This is typically accomplished using standard pH probes and meters. For basic solutions (pH >7), the pH increases as the concentration increases due to a decrease of H^+ ions in solution. This is demonstrated in Figure 2 for various common bases.
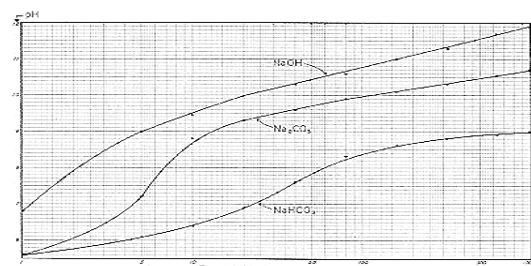

Figure 2: pH vs Concentration for various bases

In this study, conductivity and pH sensors were used to monitor the concentration of KOH under various processing conditions. These included IPA, Si content and various additives in the KOH bath. Results showed that the etch by-products do not affect the linear conductivity (or pH)-concentration relationship, nor did any of the additives. However, based on the chemical reaction for the anisotropic etching of silicon [6], it is well known that KOH gets consumed during the etching process. The consumption of KOH with added silicon thereby results in a change, i.e. decrease, in both conductivity and pH.

Since the addition of silicates in a bath has the ability to affect the process results (e.g. etch rates and texturization), the KOH concentration sometimes needs to be incremented or 'ratcheted' up for each production lot [7]. Using the conductivity data, an algorithm can be developed for ratcheting the KOH concentration in order to obtain consistent results. As such, the etch kinetics and bath dynamics can be precisely maintained using cost-effective monitoring sensors (conductivity) and SPC algorithms.

While both methods, conductivity and pH, showed a correlation with KOH concentration, conductivity was found to show the most promise. The change in pH with concentration is very small and the pH electrode is less accurate for what is required for chemical concentration control.

2. EXPERIMENTAL

For the initial characterization of the process, experiments were conducted on a small scale (≤6L) using an in-line conductivity sensor within the recirculation loop of the apparatus. Data was collected with and without automatic temperature compensation (ATC). Off-line pH measurements were carried out using a Denver Instruments Auto-Titrator with a combination pH electrode and adjusted for temperature compensation. Chemical mixes included KOH, KOH/IPA and KOH/IPA-free additives. Mixtures were also loaded with various silicate levels by dissolving bare Si p-type wafers in solution. Concentration measurements were validated using independent off-line titration methods. The characteristic curves of conductivity versus silicon loading and KOH concentration were developed and used as key parameters for the control scheme.

For testing the control method, experiments were conducted on a fully-automated GAMA™ wafer etching and cleaning system. Measurements of concentrations were taken using inline conductivity and NIR (near Infra-Red) sensors located within the recirculation loop of the process tank. Production lots of 30-50 silicon wafers at a time were processed in a tank consisting of KOH/IPA-free additive at 90ºC. The bath was adjusted prior to each lot (i.e. pre-lot spike) in order to maintain a consistent etch rate and obtain complete texturization of the wafers. Results were compared to the theoretical model that had been developed.

3. RESULTS AND DISCUSSION

3.1. KOH Concentration

Figures 3 and 4 show the results of a design of experiment (DOE) with different additives, KOH concentrations and temperatures. The data in Figure 3 shows that when no temperature compensation is employed, the conductivity increases with increasing temperature. This is expected as the mobility of ions will increase at higher temperatures. However, when ATC is employed the conductivity gets related back to a reference temperature (25ºC) for easy comparison between samples. As can be seen, the data with ATC shows an increase with increasing KOH concentration but remains relatively stable with increasing temperature. For the purposes of these experiments, a linear temperature compensation was enabled within the conductivity meter. Since production processes may run at different temperatures depending on the situation, using ATC is the simplest method in order to develop an algorithm suitable for the various processes that may be encountered.
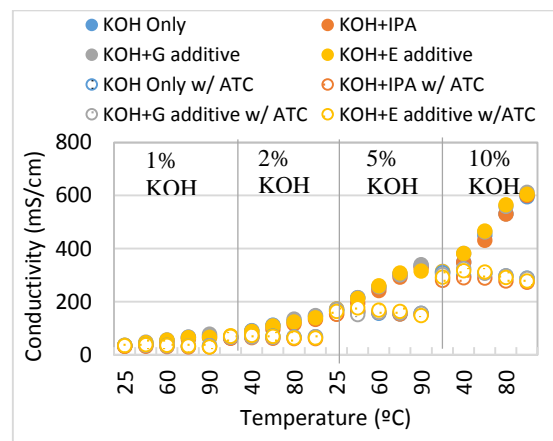

Figure 3: Conductivity vs Temperature for Differing KOH Concentrations w/ and w/o ATC

Figure 4 shows the results of the DOE on pH. As can be seen, the pH increases with increasing KOH concentration but remains relatively stable with changes in pH.

The conductivity and pH data for the DOE did not show any significant affects from the addition of IPA or the various additives. This suggests that using conductivity and/or pH as a monitoring and control method for KOH can be a viable alternative to the current methods being employed since the response will be due to changes in KOH only.
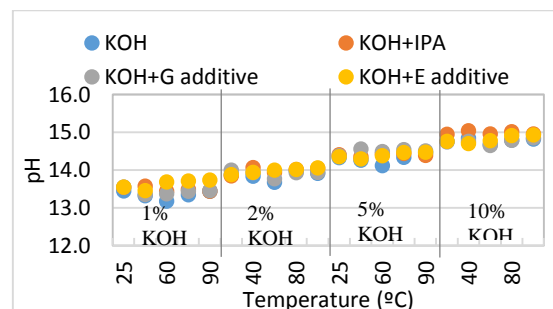

Figure 4: pH vs Temperature for Differing KOH Concentrations

Figure 5 shows the average conductivity and pH (from Figs 1 and 2) as a function of KOH concentration. By calculating the slope of the line, the conductivity and/or pH at varying concentrations can be determined as follow:

$$Cond \ (or \ pH)_n = (KOH_n * m_1) + b$$
(eq. 1)

Where m_1 is the slope of the line and b is the y intercept. Using the information from Figure 5, the conductivity and pH at a KOH concentration of 2% would be 67.78mS/cm and 13.709, respectively. These values are close to experimental values of 68.76mS/cm and 13.860.

The data in Figure 5 can also be used to determine a step-wise increase (i.e. ratchet) in KOH concentration. This is often required in order to maintain consistent results (i.e. etch rate and texturization) since increased silicate levels in the bath can adversely affect the etching process. As such, an algorithm was developed based on the data in Figure 5.

A step-wise increment in KOH concentration can be calculated from conductivity as follows:

$$\Delta Cond_{incr} = m_1 * \Delta KOH \qquad \text{(eq. 2)}$$
$$Cond_{n+1} = Cond_n + \Delta Cond_{incr} \qquad \text{(eq. 3)}$$

Where m_1 is equal to 29.215 (Fig. 5). Based on equations 2 and 3, if the KOH concentration needed to be increased by 0.50% for each lot due to increased silicate loading and the initial conductivity was 150mS/cm, the new conductivity set point would be 164.61mS/cm.
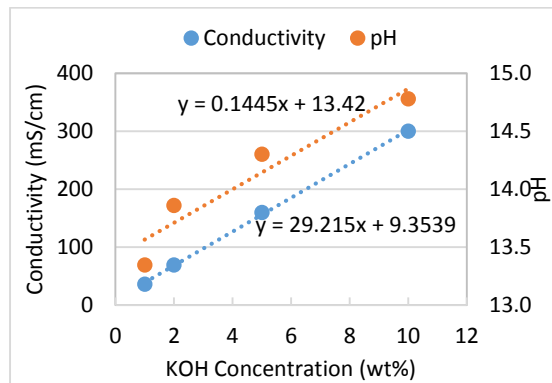

Figure 5: Conductivity and pH vs KOH Concentrations

3.2. Silicate Loading

Figures 6 and 7 show the effects of silicate loading on conductivity and pH, respectively. As silicon is dissolved into the bath, both conductivity and pH decrease as KOH is being consumed. The drop in conductivity with added silicon can be calculated as follows:

$$\Delta Cond_{drop} = m_2 * Si_{add} \qquad \text{(eq. 4)}$$
$$Cond_{n+2} = Cond_n + \Delta Cond_{drop} \qquad \text{(eq. 5)}$$

Where m_2 is equal to -3.899 (Fig. 6).

Since the dissolved Si does not appear to affect conductivity, the KOH conductivity set point can be entered as a tank parameter at the start of the process on a fresh bath. By doing so, the bath will automatically adjust using the in-situ chemical concentration control system (ICE™) in order to always maintain to the desired set point. However, if multiple production lots are to be run and the bath loaded with silicon, the KOH may need to be ratcheted up with each lot as described earlier (eqs. 2-3).
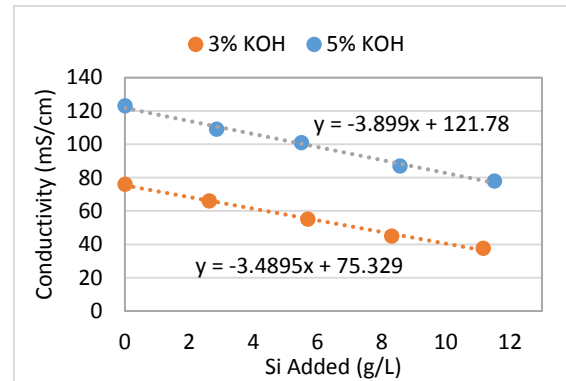

Figure 6: Conductivity vs Si Added for Various KOH Concentrations

Figure 7 shows the change in pH with added silicon for two different starting KOH concentrations. As can be seen, the change in pH is relatively small with added silicate loading. It was also found that the accuracy of the pH electrode may not be adequate enough or the reading stable enough to reliably detect small changes in concentration. As a result, conductivity would be the more suitable method for concentration control of the bath.
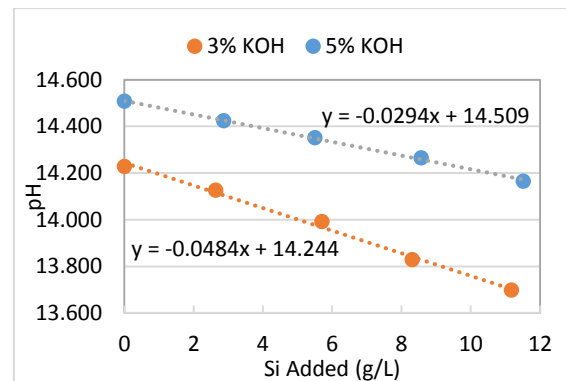

Figure 7: pH vs Si Added for Various KOH Concentrations

3.3. Validation Testing

Figure 6 shows the results of actual production runs on a fully automated GAMA™ tool using KOH with G additive (i.e. IPA-free). A KOH spike was added before each run (pre-lot spike) based on the expected amount of Si etching to occur. As can be seen, the conductivity after etching for each lot fell back to the original value. This control scheme resulted in consistent etch rates and complete texturization for all wafer lots.
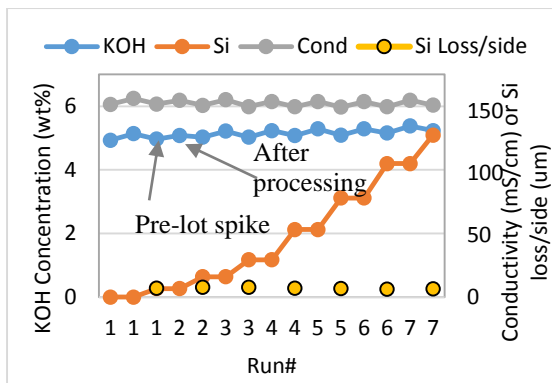
Figure 8: Conductivity vs Si Added with Replenish for Actual Process

Using the information in Figures 3 and 4 along with equations 2-5, a comparison of actual versus theoretical conductivity for the productions runs was developed. The results are shown below in Figure 7. The theoretical values during spiking and consumption compare closely to the actual values (error is within 2mS/cm).
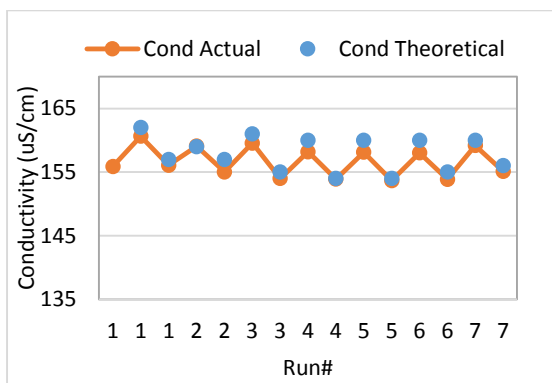

Figure 9: Theoretical vs Actual Conductivity for Production Runs

4. CONCLUSIONS

Results showed that real-time chemical concentration control by conductivity could be beneficial for advanced solar cell manufacturing. The development of an empirical relationship between bath conductivity and silicate loading as well as KOH concentration was found. Validation testing of the new system to retain stable etch rates in a KOH bath (with IPA-free additive) has been conducted on a GAMA™ Solar tool. The experiment demonstrated the effectiveness of the new control scheme in achieving stable etch rates and complete texturization over the course of multiple production runs. As a result, these low-cost, real-time measurements will significantly enhance the robustness of wafer processing. More importantly, it will increase the uptime of equipment, lower the COO and tighten the control bands of the process window.

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