Monitoring of Wet Etch for Wafer Thinning and Via Reveal Process

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Abstract

TSV (Through Silicon Vias) are usually formed and deposited as blind vias. As a last stage, vias are opened by thinning of the back side of the wafer. While the bulk of the silicon can be removed by both wet and dry methods, the final step of the "Via Reveal" process is predominantly performed by wet etch.

Two commonly used types of etching solutions are anisotropic alkaline etch (KOH, TMAH, etc.) and isotropic etch (HF/HNO3, etc.). Etch rate, uniformity, and product characteristics strongly depend on the composition of solution: both original compounds and reaction products.

This presentation describes different approaches for process control of both alkaline and acidic etch solutions using advanced spectroscopic models and potentiometry. Pros and cons of different approaches are discussed. Specific emphasis is placed on the monitoring of reaction products.

Key words

Electrochemistry, NIR, Multivariate Analysis, Silicon Etch, and TSV reveal.

I. Introduction

TSV (Through Silicon Vias) are usually formed and deposited as blind vias. As TSV integration flows, the back side of the wafer must be thinned, and the bottom of TSV must be revealed to make additional contact. In general, there are four primary wafer thinning techniques: mechanical grinding, Chemical Mechanical Polishing (CMP), Atmospheric Downstream Plasma (ADP), Dry Chemical Etching (DCE), and wet chemical etching [1]. Among these four techniques, wet chemical etching is widely used for wafer thinning and the via reveal process.

Based on chemicals used in wet etching, this process is categorized into two divisions: acid etching and alkali etching. In isotropic acid etching, a solution of mixed acids, usually HF and HNO_3 blend, is used. It is a two-stage reaction with silicon. The first step is to oxidize Si by HNO_3, and the second step is to remove SiO_2 by HF. The concentrations of both acids affect the etch rate [2].

$$4HNO_3 + 3Si \rightarrow 3SiO_2 + 4NO + 2H_2O \quad (1)$$
$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \quad (2)$$

In anisotropic alkali etching, either KOH or TetraMethylAmmonium Hydroxide (TMAH) is used as the etchant. The etching reaction is as follows:

$$Si + 4OH^- \rightarrow Si(OH)_4 \downarrow + 4e \quad (3)$$
$$2H_2O \rightarrow 2OH^- + H_2 \uparrow \quad (4)$$

Composition of the etchant, including original compounds and reaction products, have significant impact on etch rate, uniformity, and characteristics of the final product. This paper focuses on challenges and solutions to monitor these silicon etchants in a real-time manner. In the wafer thinning process, a large quantity of Si is etched and dissolved in the etching bath. Comparatively, in the TSV reveal process, the amount of Si from the etched wafer is much smaller. Therefore, it is more challenging to measure the etched/dissolved Si in the TSV reveal process.

Electrochemistry methods like titration and potentiometry are widely used to determine acid/base concentrations. In a simple matrix containing only one acid/base, titration can provide good results. For a multi-component matrix, e.g. HF/HNO_3 etchant, additional steps using reagent and/or a particular electrode are usually needed. These methods have good accuracy and reproducibility. In addition, etched/dissolved Si also has a separate transition on the titration curve. It can be used to determine the Si concentration quantitatively. The Si concentration can affect etching bath performance, such as etch rate, bath lifetime, etc. The capability to measure Si concentration has great potential for tight process control and bath lifetime extension. The drawback of this method is the time consuming titration steps. Even for an automated procedure, it usually takes 5 to 15 minutes to obtain one result. Thus, this method is insufficient for real-time etching bath monitoring.

Considering the high throughput in the semiconductor industry, real-time monitoring is always preferred as compared with offline bench analysis. In addition, real-time sensors avoid human contact with these chemical and/or thermal hazardous solutions [3], [4]. In particular, near-infrared (NIR) spectroscopy is very promising for this application in several aspects: 1. Fast in-line measurement provides real-time results; 2. Non-contact with chemicals; 3. Concentrations of multiple components can be obtained from a single spectral scan by multivariate analysis.

In NIR spectroscopy, poor correlation is usually found between absorbance at any single wavelength and analyte concentrations. Thus, a more sophisticated multivariate calibration is established with multiple coefficients, and each coefficient corresponds to a single wavelength. The analyte concentration is expressed as:

$$c_{analyte} = c_{\lambda_1} \times A_{\lambda_1} + \cdots c_{\lambda_i} \times A_{\lambda_i} + \cdots c_{\lambda_n} \times A_{\lambda_n} \qquad (5)$$

where c_{λ_i} is the coefficient at wavelength λ_i and A_{λ_i} is the absorbance at wavelength λ_i . The coefficient set is predetermined by a large amount of calibration data and multivariate analysis.

Calibration models for all of the previously mentioned Silicon etchants have been successfully established. Performance in the Si etching process is also evaluated. With NIR spectroscopy, multiple components in the Si etching solutions can be measured with fast, accurate, and repeatable results.

II. Experimental Results and Discussion

A. *Titration Method*

Titration was performed using an ECI QualiLab® auto-titrator with a pH electrode as indicator. 1.00 N HCl or 1.00 N NaOH was used as the titrant. Fig. 1 shows a typical titration curve when titrating KOH of various concentrations. Sharp endpoint volume can provide excellent accuracy and reproducibility for this measurement. There are two methods to introduce silicate into the solution: (i) artificial introduction of silicate salt as illustrated in Fig. 2 and (ii) actual etching of Si in hydroxide solution as illustrated in Fig. 3. Silicate hydrolyzes in water releasing extra hydroxide:

$$SiO_3^{2-} + H_2O \rightarrow HSiO_3^- + OH^- \qquad (6)$$

The first transition (V_{end1}) corresponds to titration of hydroxide present in solution:

$$OH^- + H^+ \rightarrow H_2O \qquad (7)$$

The second transition (V_{end2}) corresponds to titration of hydrosilicate:

$$HSiO_3^- + H^+ + H_2O \rightarrow Si(OH)_4 \qquad (8)$$

Thus, both components can be determined from a single titration. This assignment corresponds to true concentration of components present in solution (hydroxide and hydrosilicate). However, if the amount of raw ingredients required to form this hydroxide is desired, additional transformation is required:

$$OH^-_{added} = OH^-_{measured} - Si_{measured} \qquad (9)$$

Molar concentration units should be used in this transformation.

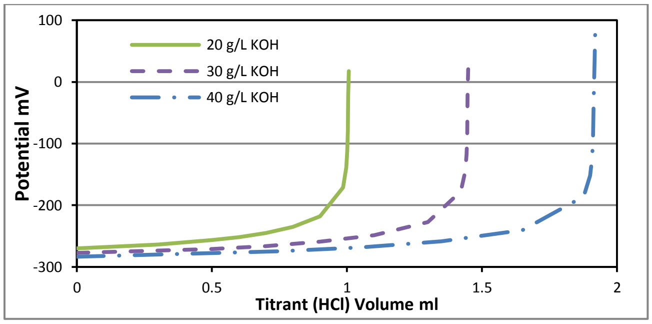

Figure 1: Titration curves of KOH base etchant by HCl

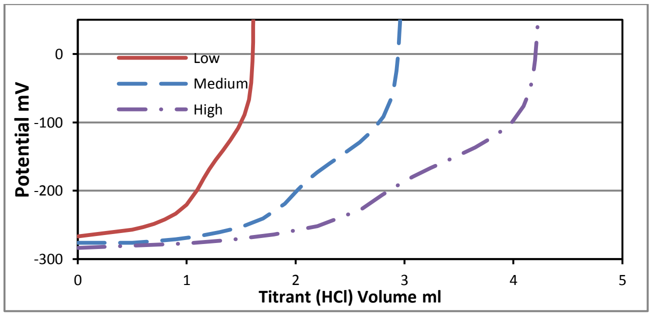

Figure 2: Titration curves of KOH base etchant containing different amount of dissolved Si by HCl: low has 7 g/L Si and 20 g/L KOH, medium has 14 g/L Si and 30 g/L KOH, and high has 20 g/L Si and 40 g/L KOH.

In an etching process, the same titration was performed on fresh KOH etchant, etchant after two hours etching, and etchant after four hours etching. The titration curves are shown in Fig. 3. They all have the same final endpoint V_{end1}. Since these samples were from the same bath, the OH^-

concentrations are the same. The other endpoint (V_{end2}) varies for etchants with different etching time. As discussed previously, V_{end2}-V_{end1} determines the etched/dissolved Si.

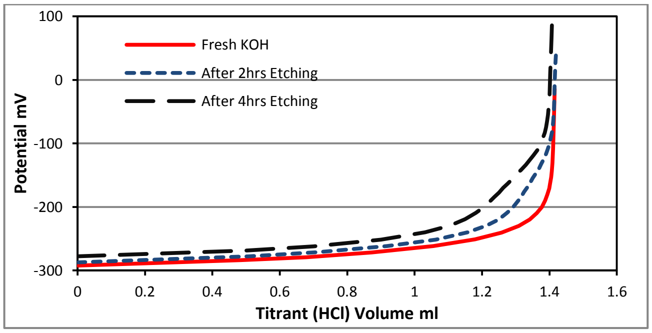

Figure 3: Titration curves of KOH etchant with various etching time

When a solution of mixed HF/HNO_3 acids is titrated by NaOH, unfortunately the titration curve (Fig. 4) only shows one endpoint. This means titration by NaOH can only measure the total amount of acid. Additional titration with $La(NO_3)_3$ is performed using a fluoride ion selective electrode (ISE) (Fig. 5). The reaction is as follows [5]:

$$La^{3+} + 3F^{-} \rightarrow LaF_3\downarrow \quad (10)$$

This step determines the HF concentration. Then the HNO_3 concentration can be obtained by either calculation (by subtracting the HF concentration from the total amount of acid obtained from previous step), or UV-VIS spectroscopy. Similar to base etchant titration, the Si dissolved in the format of SiF_6^{2-} also shows a separate transition on the titration curve, and the Si concentration can be obtained in the same way [6].

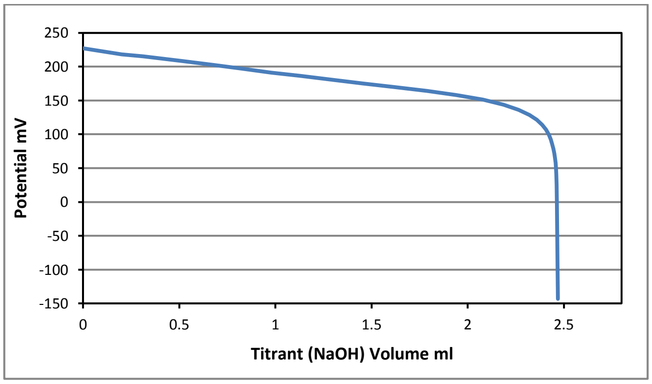

Figure 4: Titration curve of HF/HNO_3 acid etchant by NaOH

The titration method just discussed can measure etched/dissolved Si in the g/L range. This is suitable for the monitor wafer thinning process, but in the TSV reveal process, etched/dissolved Si may only reach ppm level. This titration method is not sensitive to such a low level of Si. An alternative potentiometric method was developed for ppm level Si in TMAH etchant. Fig. 6 shows a good correlation between the electrode response in mV and Si concentration in a range of 0-200 ppm.

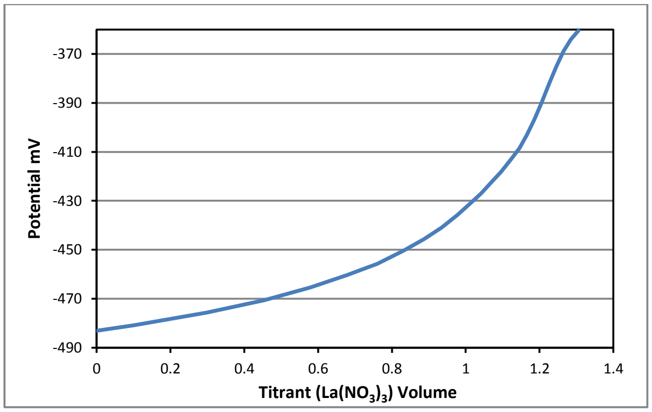

Figure 5: Titration curve of HF/HNO_3 acid etchant by $La(NO_3)_3$

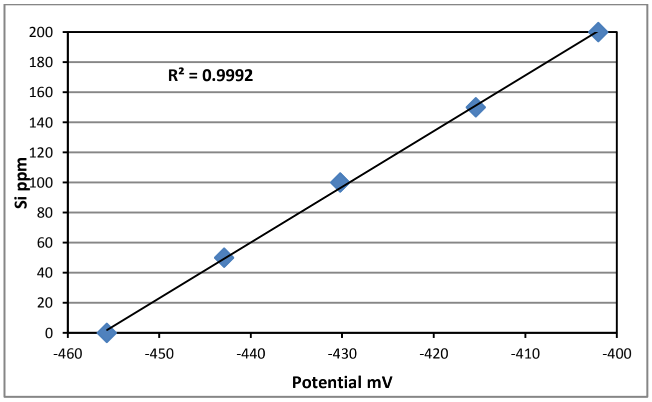

Figure 6: Measure potential vs. expected Si concentration in ppm

Titration methods developed in this study are capable of measuring all components in silicon etchants, plus the dissolved/etched silicon. With additional automation, this method can be implemented for online analysis, where the time resolution is not critical. Also, titration performance is stable in the long term, and drift is usually not a concern.

B. NIR Spectra

NIR spectra of both TMAH and HF/HNO_3 solutions were collected under various temperatures using an ECI QualiSurf® analyzer. As shown in Fig. 7 and 8, the dominant peak is from the first overtone of O-H stretch. In aqueous solutions, this O-H band is heavily affected by the nearby hydrogen bond. In Fig. 7 and 8, it can be clearly seen that acids, bases, and temperature have significant impact on this O-H band, in respect to both magnitude and peak position. Therefore, this O-H peak is used to quantify acid/base concentrations in this study. However, no good correlation between concentrations of analyte and any single wavelength can be found. Simple univariate method would not work in this case. A multivariate model described in equation (5) is used for calibration models. Spectra of a variety of samples with different mixing ratios were collected.

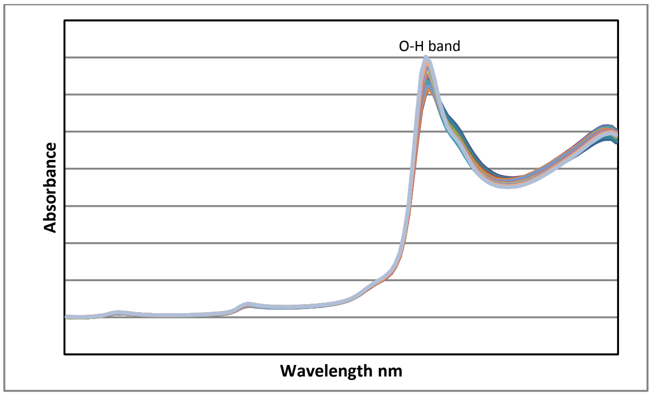

Figure 7: NIR spectra of HF/HNO_3 acid etchant with different mixing ratios at different temperatures

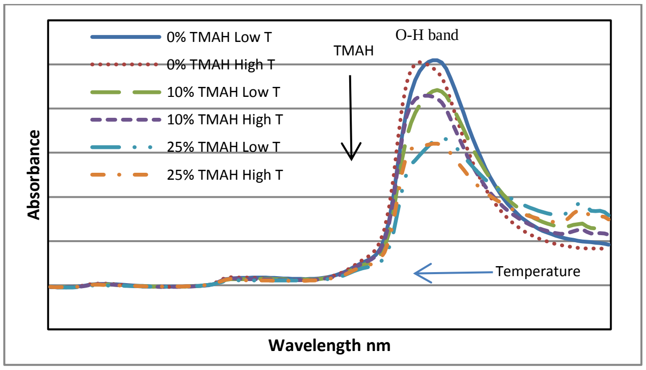

Figure 8: NIR spectra of TMAH with different concentrations at different temperatures

C. *Multivariate Analysis (MVA) Results*

To create good quantitative models for these analytes, multivariate analysis and/or certain spectral pre-processing methods were used. Performances of these calibration models are shown in Fig. 9-12. Results shown demonstrate good accuracy and reproducibility for TMAH, HF, HNO_3, and H_2O. In addition, all of these results demonstrate good stability over certain temperature variations. This is very important for real time inline monitoring process, because the batch temperature can fluctuate due to the process, and solution temperature may also vary by the time it goes though the measurement cell. A robust real time analytical method should be able to work with certain temperature fluctuations.

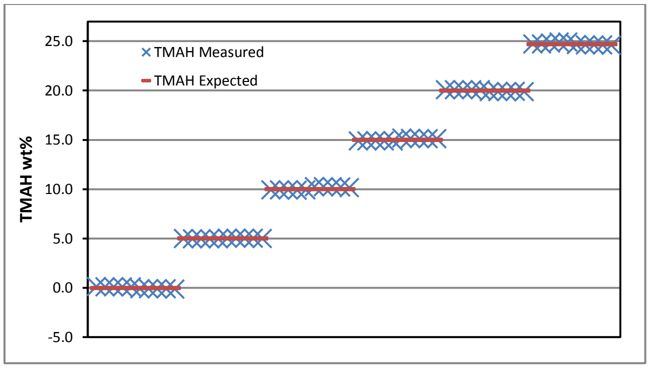

Figure 9: TMAH resutls: expected and measured

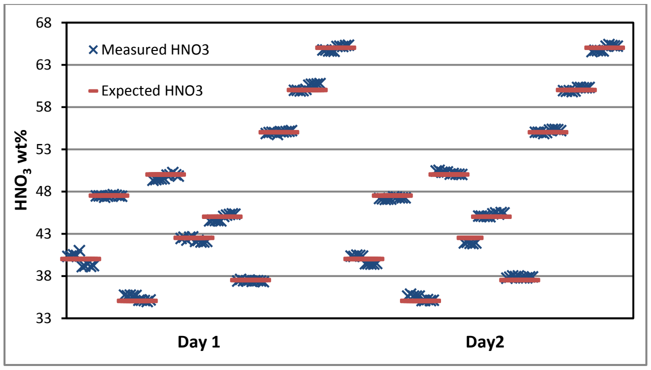

Figure 10: HNO_3 results: expected and measured

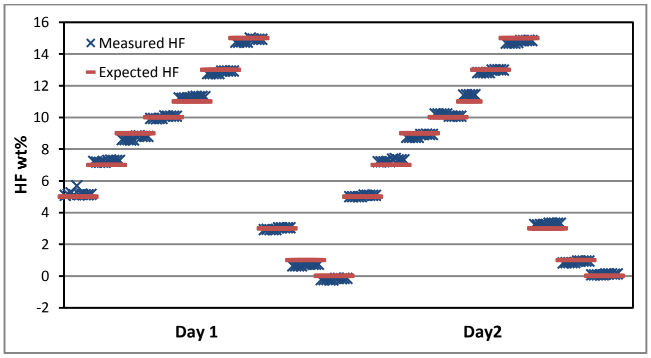

Figure 11: HF results: expected and measured

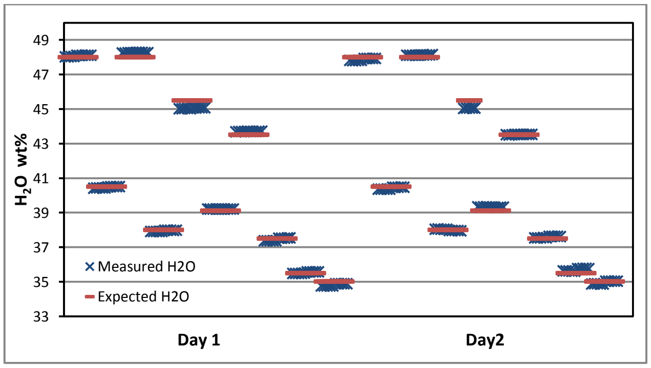

Figure 12: H_2O results: expected and measured

NIR spectroscopy method developed in this study can provide real-time results for each componet in the etchant. While the etchant solution continously flows through the measurement flow cell, the NIR spectra are collected continously. Thus, real-time data is obtained. Over time, any spectroscopy based method suffers from optical drift. The previously developed titration methods can provide additional validation results to compensate for the drift in results caused by optical instability.

III. Conclusion

In this study, both titration and NIR spectroscopy methods were developed to quantitatively determine the individual components in both acid and base etchants. Each method can work independently for Silicon etching bath control. They can also be combined to provide both real-time results and long-term performance.

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