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APPLICATION NOTE

NIR Spectroscopy to Monitor Cleaning Solutions in Semiconductor Wafer Manufacturing Process

Introduction

In a competitive semiconductor industry, where high volume and maximum efficiency mean everything, an emerging technology commonly used in the chemical and refining industries may be a suitable processing aid. Process Near Infrared (NIR) spectroscopy generates rapid, real-time data that is reliable and easily interpreted. Engineers, scientists or operators may use this information to fine tune a process, resulting in more efficient use of materials while still maintaining high product yields.

Some unique Process NIR features include real-time analysis, in situ or non-invasive sampling possibilities, and multi-point capability. The sample loop consists of specialized fiber optic cable and a sampling interface allowing for remote placement of the analyzer. This provides a convenient alternative when consideration must be given to the processing environment, i.e. clean rooms, or to operator safety during analyzer system servicing.

Arguably the backbone of the Electronic Industry is the intergrated circuit chip. As researchers continually develop techniques to embed smaller and faster circuitry onto silicon surfaces, the more crucial become the cleaning and etching procedures. Most wafer manufacturers use wet chemical cleaning to carry out these functions. The success of cleaning steps, either pre- or post-etch, is largely gauged by, the cost of chemicals, cycle times, and the yield product wafers-per-batch. Optimal bath conditions are easily determined through experimentation. The real challenge comes when trying to keep the conditions constant during production. At the very least, significant chemical changes result from the chemical cleaning action and evaporation of the solution (wafer cleaning often occurs at bath temperatures around 80 °C). Currently used on-line conductivity methods can be effective to characterize solutions, but can not be accurate for three-component solutions or greater. Taking a periodic grab sample to the lab is not feasible due to the associated lag time. Process NIR can rapidly and accurately assess bath condition and instantaneously signal for bath replenishment when it is required.

Of the many wafer cleaning and etching solutions in use today, "SC-1"and "SC-2" are the most common. These are commonly referred to as the standard cleaners. SC-1 is comprised of one part 30% ammonium hydroxide (NH_4OH) solution, one part 30% hydrogen peroxide (H_2O_2), to five parts ultra pure de-ionized (DI) water. SC-2 is similar in composition, substituting only 37% hydrochloric acid for the basic NH_4OH present in SC-1. Other type solutions include aqueous mixtures of sulfuric acid (H_2SO), phosphoric acid (H_3PO_4,), hydrofluoric acid (HF), and hydrochloric acid (HCl). Unfortunately, the list of wet chemical cleaners is growing faster than the development of means to accurately analyze them.
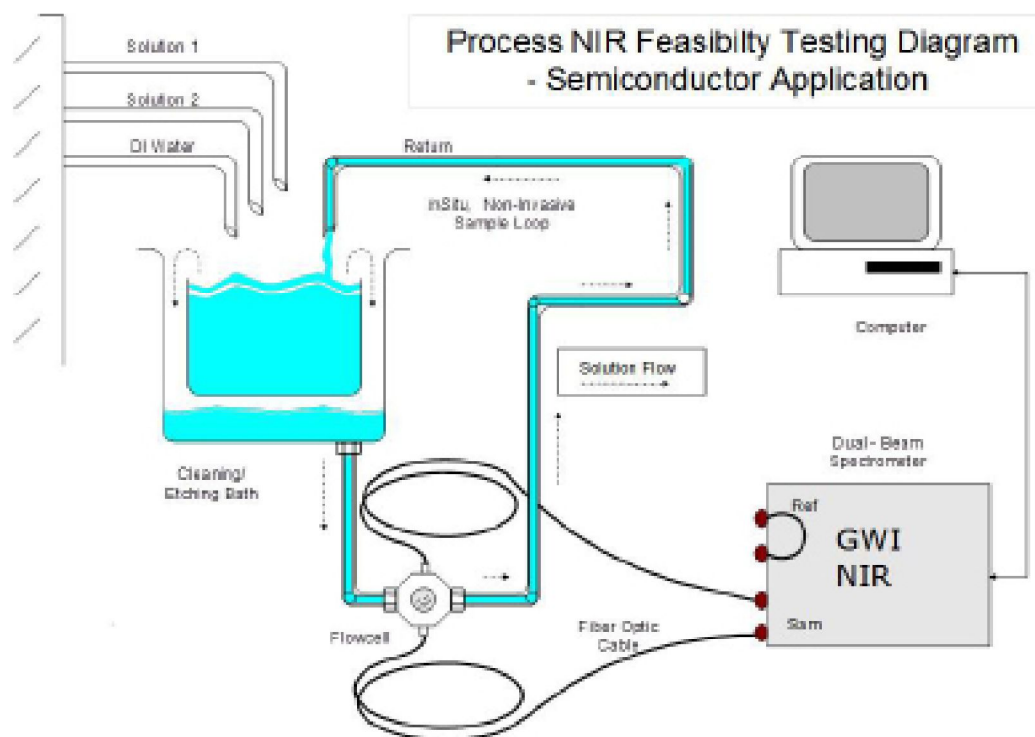
Figure 1: Diagram of Experimental Test Configuration.

Experimental Setup

For wafer cleaning and etching, bath tables consisting of several circulating baths are very common. Each bath has separate controls for temperature and circulation adjustment. And the design provides continuous micro-filtration to remove contaminant particles from solution. For processing, wafers are placed into non-metallic slotted baskets specially designed for submergence into the various cleaning/ etching solutions.

Most of the procedural steps involved are automated and baths are typically located in "clean room" environments.The great disdain given in the research literature for metallic parts prompted the use of a special Teflon sample interface. Our experiments intended to simulate, as best as possible, "real world" wafer processing. The list of major apparatus and an experimental setup diagram are shown in Figure 1.

Experiment

- GUIDED WAVE NIR analyzer
- 2 - 6 meter length jacketed fiber optic cable, 500 micron
- Teflon flow cell, with 2 mm pathlength
- Cleaning bath, 57 liter capacity, overflow/recirculating design

Test Solutions

Six different bath solutions were studied in separate experiments. They are listed in Table 1.

Solution Components	Typical Mixture Ratio
30% NH4OH : 30% H_2O: H_2O (SC-1)	1: 1: 5
37% HCl : 30% H_2O_2 : H_2O (SC -2)	1: 1: 5
49% HF : H_2O	1: 100
49% HF : 30% HCl : H_2O	1: 1 : 100
96% H_2SO_4 : H_2O	4: 1
96% H_3PO_4 : H_2O	4: 1

Table 1: Cleaning /Etching Bath Types Studied.

Approach

Experiments were designed to assess the feasibility of NIR spectroscopy for solving problems associated with the continuous operation of automated cleaning/etching baths. One major challenge in operating wet chemical cleaning processes is maintaining optimal bath conditions required to insure uniform cleaning, reduced cycle times and minimal product rework. As an added benefit, accurate analysis would make the most efficient use of costly ultrapure chemicals, and reduce chemical waste.

Thus far, the industry has survived relying on two moderately effective analytical techniques to monitor baths. Some baths are equipped with semi-continuous conductivity meters. Although fairly accurate in the analysis of binary solutions, these instruments are incapable of accurately monitoring multi-component systems. The other option is to send a grab sample to the laboratory. Lab results are usually very reliable, but the associated lag time makes this alternative impractical. Process NIR is a logical solution provided the success achieved in other industries could be duplicated.

Six bath solutions were selected for evaluation on the basis of popular use and effective chemical cleaning or etching action. Our experiments involved initial preparation of a test bath at target starting concentrations, and then adjusting component concentrations in steps to predetermined levels. After a period to allow the bath to equilibrate, spectra were collected at each interval. Several spectral treatment algorithms were tried in search of a practice that would produce the most definitive and robust calibration set.

A third party chemometric software package was used to analyze the multivariate data. For each experiment, the set of calibration samples (spectra) was used to generate a partial least squares (PLS) calibration model. Each model was then applied to the very same spectral objects from which they were developed. Predictions were made with reference to the measured concentrations and statistically evaluated within the framework of the chemometric package. Much statistical analysis was performed on both the calibration and the results. The standard error of prediction (SEP) was used as the primary success criteria.
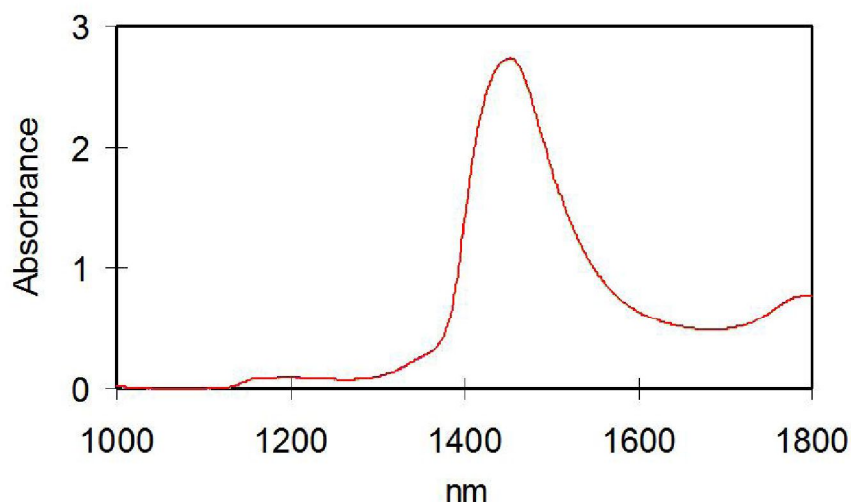
Figure 2: Raw SC -1 Specta Collected with an Air Reference.

Results and Discussion

In the first experiment, 16 defined intervals of SC-1 solution were prepared by automated dispensing of the solution components. The base formula of this cleaner is well known, as are the optimal concentration levels. During the experiment, the testing range for ammonium hydroxide (NH_4OH) level ran from virtually 0 to a little more than 4.6%. We tested across approximately the same range for peroxide (H_2O_2) concentration. Thesolution consists mainly of ultra - pure DI water that ranged from approximately 91.5% to near 100%.

The spectra were collected as four scan averages against an air reference. In the default viewing mode, the raw spectra practically overlayed one atop the others (see Figure 2). Though individual spectra were indistinguishable, we were pleased with the stable baseline and peak location. Closer investigation, with the zoom feature in the control software, revealed the differences we were looking for. An example of a particular zoomed window is shown as Figure 3.
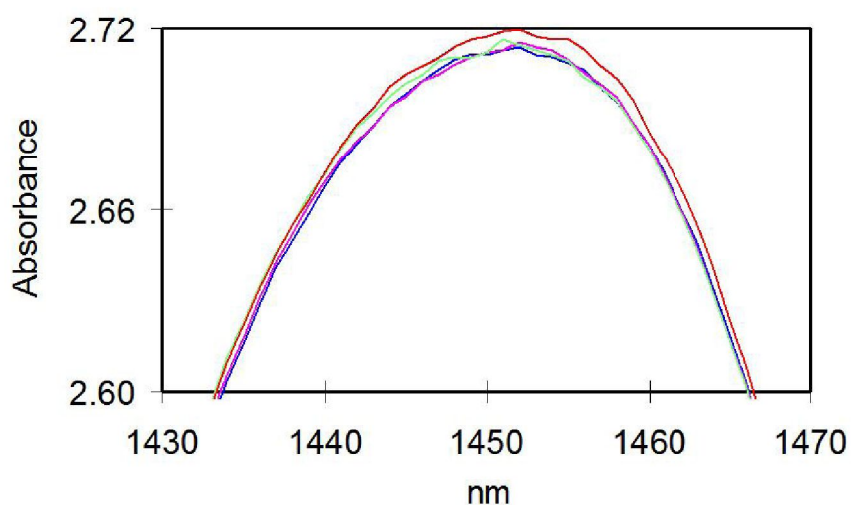

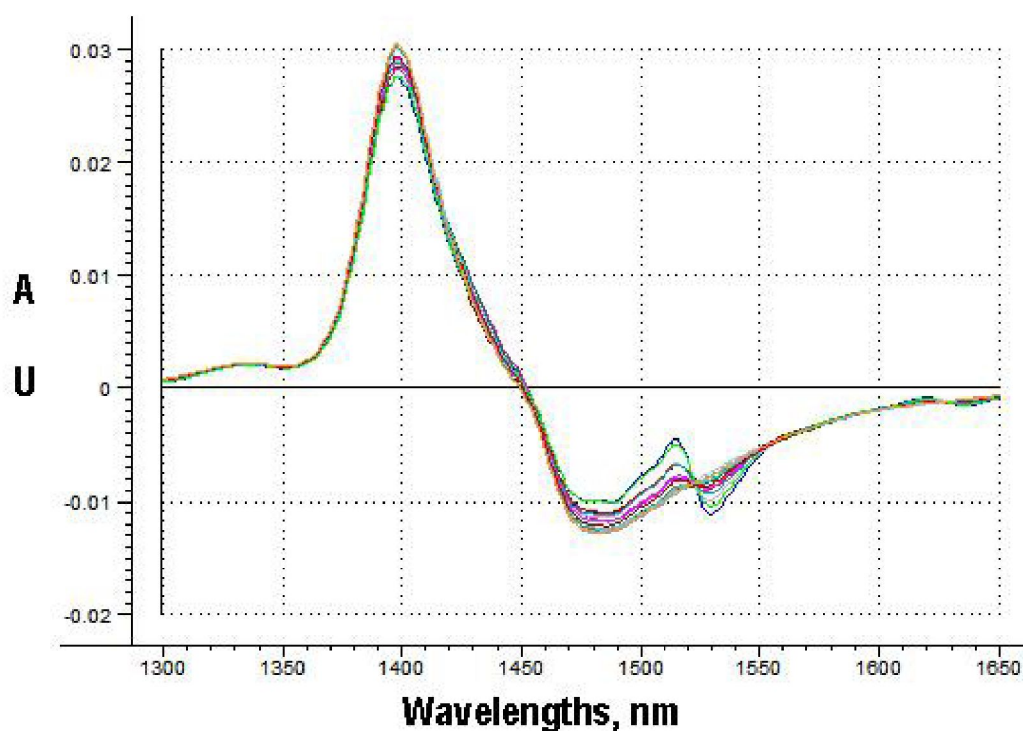Figure 3: Zoomed View of the Spctral Peak Region for SC -1 Raw Spectra.

Figure 4: First Derivatives of SC-1 Calibratin Spectra.

Results and Discussion (continued)

Review of the raw spectra defined a region from 1300 nm to 1650 nm as most suitable for modeling. Of the many spectral treatments evaluated, the first derivative seemed most effective. In addition to providing a degree of normalization, it also improved resolution of the spectral differences as depicted in Figure 4.

Using the chemometric software, PLS1 calibrations for each of the three SC-1 solution components were developed integrating all 16 spectra. After a cross validation process and analysis of the residuals, three principal components, or factors were required to adequately describe the data variations for each bath component. The calibration was tested against its own objects. Figures 5 thru 7 show the result plots.
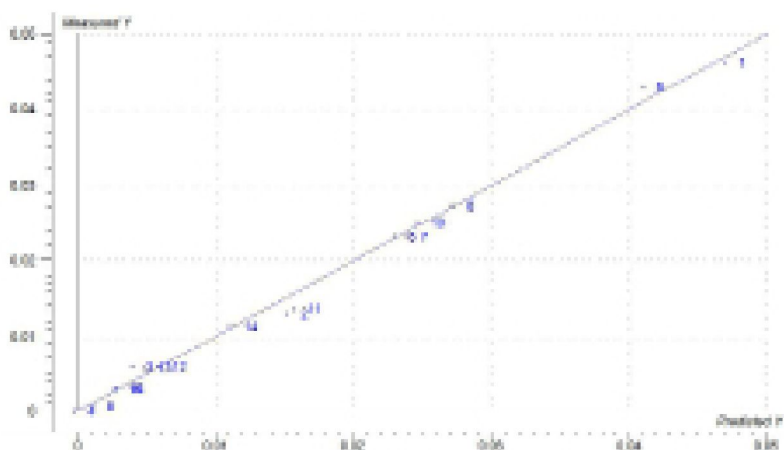
Figure 5: Measured vs. Predicted Results for % NH$_4$, OH in SC-1 Cleaning Solution.

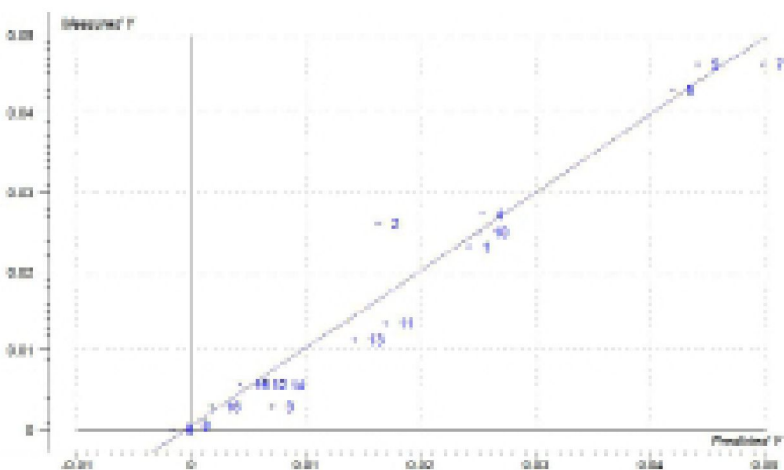Figure 6: Measured vs. Predicted Results for % H$_4$O$_2$ in SC-1 Cleaning Solution.
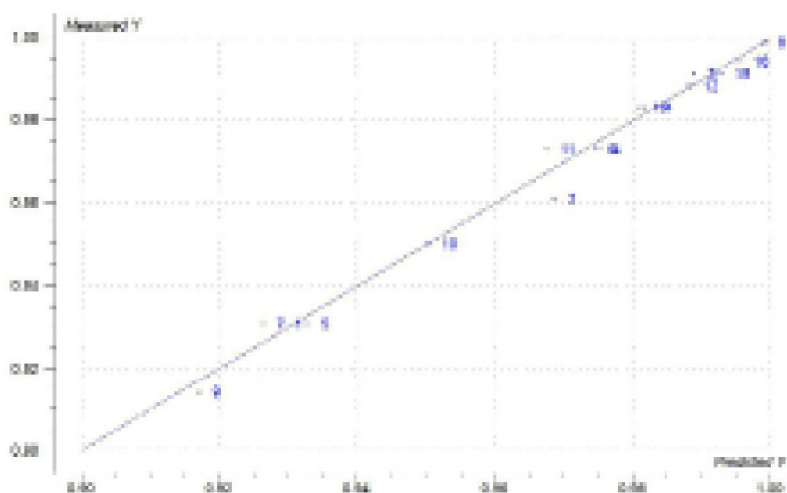
Figure 7: Measured vs. Predicted Results for % Water in SC-1 Cleeaning Solution.

Sample		NH$_4$OH (a)			H$_2$O$_2$ (b)			DI Water (c)		
ID	Mixtue Ratio (a;b;c)	Measured	Predicted	Error	Measured	Predicted	Error	Measured	Predicted	Error
1	2:1:10	4.62	4.7	-0.08	2.31	2.41	-0.10	93.07	92.89	0.18
2	5:10:100	1.30	1.52	-0.22	2.61	1.63	0.98	96.09	96.86	-0.77
3	2:1:100	0.58	0.40	0.18	0.29	0.70	-0.41	99.13	98.90	0.23
4	0:10:100	0	-0.03	0.03	2.73	2.53	0.20	97.27	97.50	-0.23
5	5:10:50	2.31	2.30	0.01	4.62	4.41	0.21	93.07	93.28	-0.21
6	10:0:100	2.73	2.72	0.01	0	-0.16	0.16	97.27	97.45	-0.18
7	1:2:10	2.31	2.39	-0.08	4.62	4.97	-0.35	93.07	92.64	0.43
8	1:1:500	0.06	0.11	-0.05	0.06	-0.03	0.09	99.88	99.91	-0.03
9	1:1:50	4.29	4.10	0.19	4.29	4.19	0.10	91.42	91.71	-0.29
10	1:1:10	2.50	2.46	0.04	2.50	2.51	-0.01	95.00	95.03	-0.03
11	1:1:20	1.36	1.57	-0.21	1.36	1.68	-0.32	97.28	96.75	0.53
12	1:1:50	0.58	0.59	-0.01	1.58	0.58	0	98.84	98.83	0.01
13	1:2:50	0.57	0.48	0.09	1.13	1.42	-0.29	98.30	98.09	0.21
14	2:1:50	1.13	1.10	0.03	0.57	0.74	-0.17	98.30	98.16	0.14
15	1:2:100	0.29	0.28	0.01	0.58	0.42	0.16	99.13	99.30	-0.17
16	1:1:100	0.29	0.27	0.02	0.29	0.18	0.11	99.42	99.56	-0.14
	Mean Error			0.00			0.02			-0.02
	SEP$_{cv}$			0.11			0.33			0.31
	Correlation			0.997			0.980			0.993

Table 2: Predicted Summary for Varied Mixture SC-1 Solutions.

Results and Discussion (continued)

For intervals where the measured concentrations approached zero, the predictions gave negative values. This often is a consequence of modelling in excess of the method or instrumentation precision; tolerable for a feasibility study. All final results show the experimental models to be suitable over industry-common ranges.

Other experiments with solutions SC-2, H$_2$SO$_4$:H$_2$O, and H$_3$PO$_4$:H$_2$O were conducted in similar fashion. The samespectral treatments and model development steps were applied. Sulfuric acidand phosphoric acid experiments wereconducted over vast ranges - from 1 to 96% by volume. The highly concentratedsolutions, prepared in 4 : 1 mixtures ofstrong acids and DI water, were successful rendering accurate predictions with low - factor PLS models.
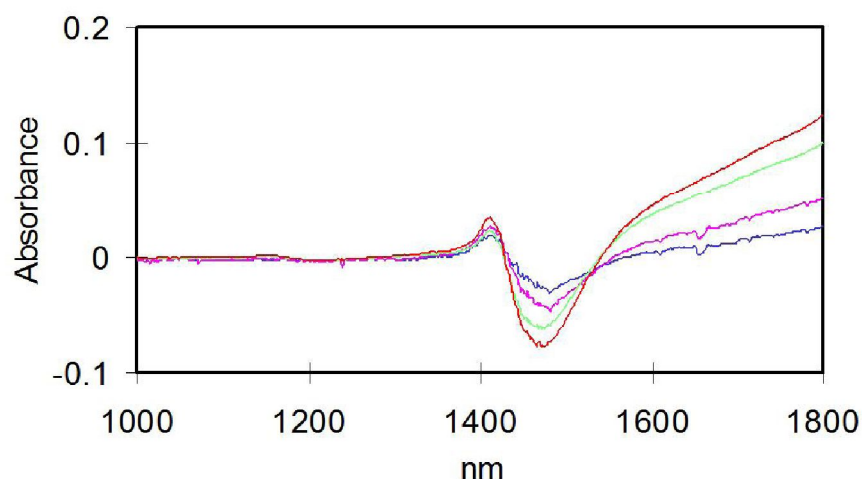
Figure 8: HF:H$_2$O Spectra with Water Reference.

Results and Discussion (continued)

Two other experiments, with typical baths HF:H$_2$O and HF:HCl:H$_2$0, were completed with some procedural changes. Instead of the air referencing used previously in this study, a water reference was employed. Also, more scans were saved at each concentration interval. First, 16 spectra were collected, then five afterevaluation of stability. To simplify mattersfurther, the subsequent spectral groups were averaged to generate a single spectrum for each concentration interval. A few of the averaged spectra are shown in Figure 8.

The water referencing was successful. The standard error of the thirteen HF:H$_2$O samples exceeded the SEP calculated during air referencing experiments by a factor of ten. It is presumed the choice and quality of reference play a major role in this application type. The result summary is provided in Table 3.
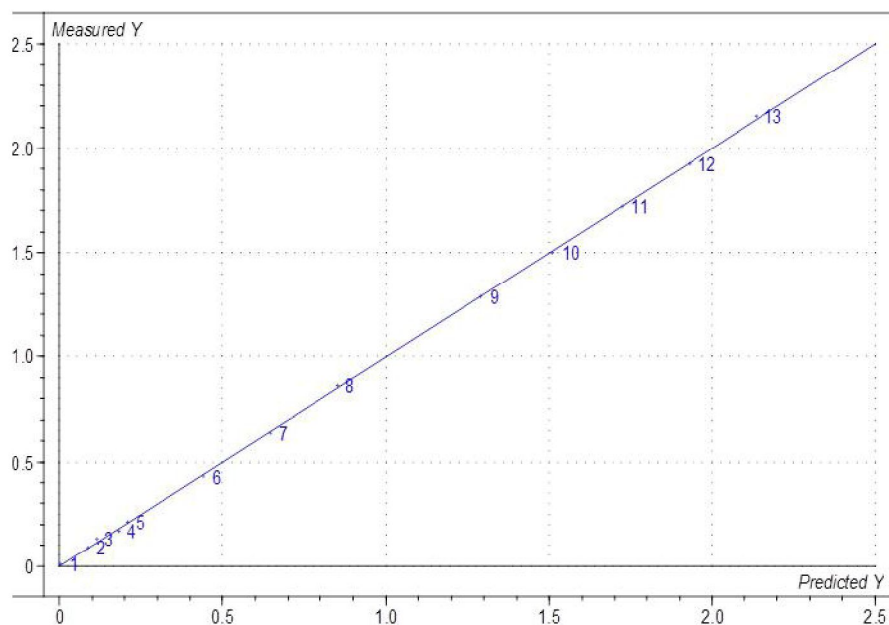

Figure 9: HF Predictions for the 13 Objects in the PLS Calibration Set.

RHF in H$_2$O

SAMPLE		NH$_4$OH			H$_2$O$_2$			DI WATER		
ID	Mixture Ratio	Measured	Predicted	Error	Measured	Predicted	Error	Measured	Predicted	Error
1	2:1:10	4.62	4.7	-0.08	2.31	2.41	-0.1	93.07	92.89	0.18
2	5:10:100	1.3	1.52	-0.22	2.61	1.63	0.98	96.09	96.86	-0.77
3	2:1:100	0.58	0.4	0.18	0.29	0.7	-0.41	99.13	98.9	0.23
4	0:10:100	0	-0.03	0.03	2.73	2.53	0.2	97.27	97.5	-0.23
5	5:10:50	2.31	2.3	0.01	4.62	4.41	0.21	93.07	93.28	-0.21
6	10:0:100	2.73	2.72	0.01	0	-0.16	0.16	97.27	97.45	-0.18
7	1:2:10	2.31	2.39	-0.08	4.62	4.97	-0.35	93.07	92.64	0.43
8	1:1:500	0.06	0.11	-0.05	0.06	-0.03	0.09	99.88	99.91	-0.03
9	1:1:5	4.29	4.1	0.19	4.29	4.19	0.1	91.42	91.71	-0.29
10	1:1:10	2.5	2.46	0.04	2.5	2.51	-0.01	95	95.03	-0.03
11	1:1:20	1.36	1.57	-0.21	1.36	1.68	-0.32	97.28	96.75	0.53
12	1:1:50	0.58	0.59	-0.01	0.58	0.58	0	98.84	98.83	0.01
13	1:2:50	0.57	0.48	0.09	1.13	1.42	-0.29	98.3	98.09	0.21
14	2:1:50	1.13	1.1	0.03	0.57	0.74	-0.17	98.3	98.16	0.14
15	1:2:100	0.29	0.28	0.01	0.58	0.42	0.16	99.13	99.3	-0.17
16	1:1:100	0.29	0.27	0.02	0.29	0.18	0.11	99.42	99.56	-0.14
	Mean Error			0.00			0.02			-0.02
	SEPcv			0.11			0.33			0.31
	Correlation			0.997			0.980			0.993

Table 3: Result Summary for HF:H$_2$O Calibration.

Results and Discussion (continued)

To evaluate model performance applied to samples outside the calibration set, an experiment was under-taken with the previously developed HF model. The bath was programmatically adjusted at predetermined levels. The test HF concentration range was within the range of the calibration model. Rendered prediction accuracy was comparable to that gathered during original model validation steps. The data plot shown as Figure 10 further substantiates this.
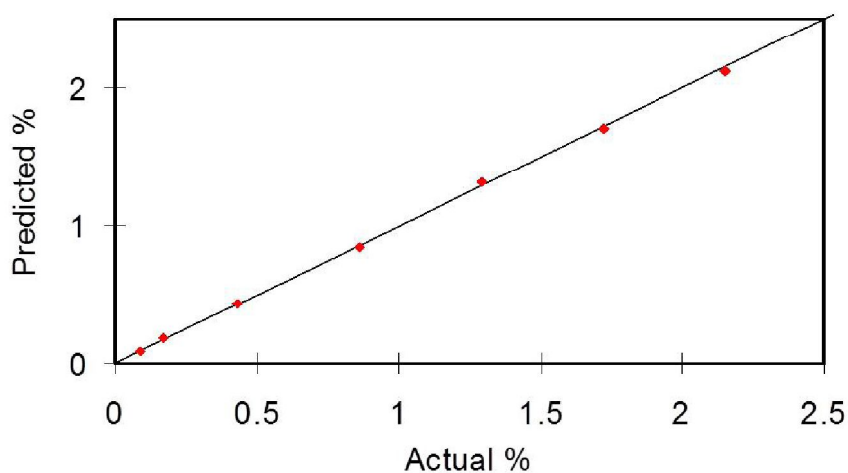
Figure 10

Results and Discussion (continued)

To approach real processing conditions, silicon wafers were added to the cleaning bath and held submerged for approximately 3 hours. Over this period, intermittent scans were collected at approximate 15-minute intervals. A typical program used to automatically replenish the bath solution operated the bath. Again, the original HF calibration model was used to make predictions. Results obtained suggest that the presence of the wafers will not significantly change the stability of neither the spectra nor the rendered prediction value. In the chart shown as Figure 11, the rise and fall represent the spent HF and corresponding acid makeup.
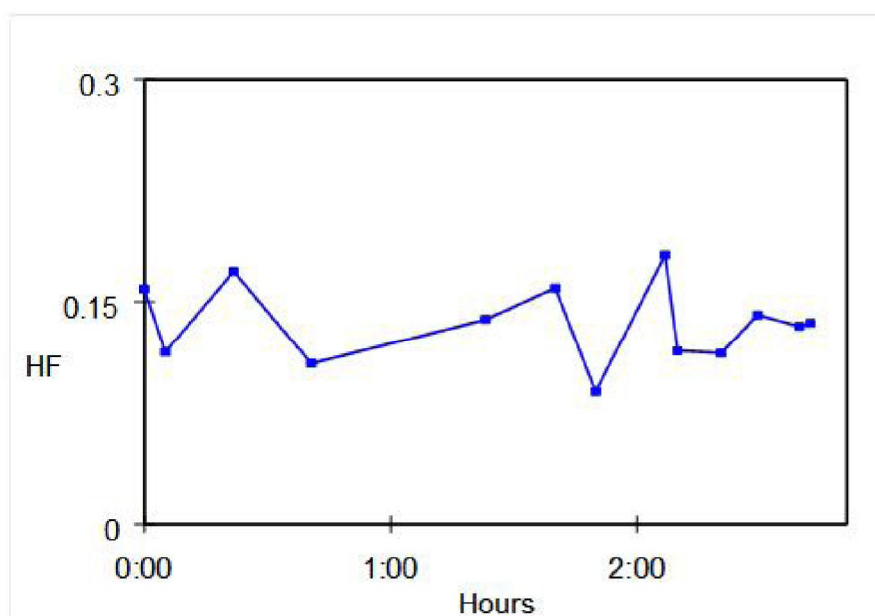

Figure 11: NIR Insitu Trend Analysis of Bath HF Concentration

Conclusion

Based on the findings, application of process NIR spectroscopy for real-time monitoring of cleaning and etching baths can provide certain advantages. Many different types of aqueous cleaning solutions can be reliably monitored. Further, this can be accomplished insitu in a real-time non-invasive, clean manner. The concept was successfully demonstrated on SC - 1, a standard clean solution under widespread use in the industry, as well as other commonly used solutions including $HF:H_2O$, SC - 2, $H_2SO_4:H_2O$, $H_3PO_4:H_2O$, and $HF:HCl:H_2O$.

Analysis for both high component concentrations, up to approximately 80%, and low levels, down to 0.1%, were determined feasible. Another recognized feature was the operational versatility provided by multi-constituent analysis. Having each solution component tracked would allow fine adjustments to continuously operate at optimal conditions.

In this study, two approaches were discovered which enhance the results. First, using a water reference for spectral measurements can be conveniently applied producing distinctive spectral regions of activity that are required for successful modeling. Also, taking a first derivative of the air-referenced spectrum has similar benefit. For levels at 0.1% or lower, statistical data smoothing looked beneficial. As expected, so did spectral baselining techniques.

For this or a similar application a Teflon flowcell is highly recommended. Our GUIDED WAVE flow cell also has sapphire windows permitting long time exposure to strong acids commonly encountered in this industry, like HF. In summation, aqueous baths of harsh acidic or basic solutions can be accurately predicted online, in real-time by spectroscopic means.

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