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# Monitoring recirculated baths using NIR inline chemical analysis

## EXECUTIVE OVERVIEW

Specialized chemical mixtures used in semiconductor processing are necessary for the surface preparation of wafers. As little as a 1% error in the dilution ratio can degrade yield in a sensitive process, both for acids and for organic solvents that contain water as a component required for the removal of etch residues. Improper water concentrations can also cause immediate corrosion and/or erosion of metals. The use of a near infrared (NIR) inline chemical analyzer enables tighter production control and reduced costs through increases in productivity, improved yields, and scrap avoidance.

**W**afer processing requires tight control of the chemical mixtures in heated baths. Diluted hydrofluoric acid (HF) baths used to etch oxides are designed to remove extremely thin layers from the surface of the wafer. HF etch-rates are specified in terms of Å/sec., and are affected by time, temperature, and HF concentration. A small error in any of the three can cause scrap in such a critical step. Since time and temperature of a specific recipe are usually constant, the wrong concentration of a chemical is usually the culprit of an improper etch.

Concentration change can occur either directly during the initial mixing of the acid/water from a failed component, or indirectly from other sources such as water carry-over from the previous rinse bath. Qualifying the bath by running an etch-rate test ensures that the right mix of acid to water is being used. Unfortunately, it is impractical to run monitor wafers constantly in a bath; in situ etch-rate tests require space, metrology time, and wafer cost. Therefore, etch-rate testing occurs anywhere from once a day to twice a week depending on the stability of the bath. If an improper mix of chemical occurs between tests, the operation runs a risk of scrapping production wafers. Additionally, running monitor wafers does not completely show chemical characteristics in an acid bath, and in a high volume production environment, equipment downtime can be an issue when searching for the root cause.

Another issue faced in a fab are baths that change acid ratio between processes. Since deployment of multiple baths for each single process is a huge cost, fabs typically design in multiple uses of single equipment,

which leads to higher process variability. For example, one recipe may need 1% HF while the following run may require a 5% mix. During the chemical exchange, carry-over from a previous bath mix can occur, diluting the strength of the acid, even if a bath clean flush with DI water is used in between exchanges.

Figure 1 shows an example of an etch-rate chart when different bath ratios were mixed, which was caused by improper draining of the DI water from the recirculation line. If the etch-rate testing frequency had been reduced on this bath, then the problem would have been invisible to maintenance personnel and production wafers would have been at risk.

## DI water in solvent checked by titration

Solvent chemicals used in post-metal semiconductor processes operate in heated tanks to remove polymers from wafers. When



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Figure 1. Improper draining of bath causes low etch from diluted acid.

solvent is delivered to the bath via a bulk chemical delivery system, its initial water concentration is too high for safe metal processing. Furthermore, in a bath that uses a water replenishment system, extending solvent bath life introduces additional risks.

To reduce these risks, a water titration system takes samples of the solvent, analyzes the solution, and provides a reading of water concentration every 30 min. Set-rate replenishment systems work well under optimal operating conditions, but they do not work well with concentration variability caused by process loadings, solvent drag-out, or tank replenishment. Use of the traditional titration analyzer provides feedback to ensure strict process control, but is limited to once every 30 min. at best. If a problem with the bath occurs between readings, as many as 150 wafers could be at risk for yield losses. Furthermore, the mechanical titration system is a high maintenance device, needing frequent preventative maintenance, parts, and titration chemicals to make it work.

### Inline monitoring of HF and solvent baths

Several different technologies for inline measuring were considered, but because accurate concentration analysis of two different chemistries can be challenging, the ideal instrument was difficult to find. An automatic inline noncontact system that remains accurate under a variety of conditions was needed. Several criteria were evaluated:

- **Type of control.** Accuracy of the device and particle contamination were major concerns.
- **Process variation.** The device had to be calibrated to measure a wide range of chemical ratios expected in the bath.
- **Electronic input and output.** External feedback from the analyzer was essential in the design of this system. The 4–20mA output signals had to interface with an online tool interdiction and monitoring system.
- **Process compatibility.** An instrument compatible with the wet chemistries of acids and solvents had to have wetted parts to be free from particle generation, and it had to contend with variable incoming pressure.
- **Ease of installation.** A drop-in unit was a priority. The automatic system had to be installed and operating quickly to prevent excessive downtime of the production equipment.
- **Multiple channels.** Cost was a factor in determining how many units were needed vs. having one multichannel analyzer that can look at multiple baths at the same time.

Methods for measuring chemical concentration include NIR, refractive, capacitive, and titration. NIR technology measures light absorbed by a fluid. Refractive uses a glass prism to break down the light spectrum, while capacitive uses electrical conductivity or

impedance to correlate chemical make-up. Titration is the traditional method of using chemical reagents to react with water in a sample of a solution and measuring an electrical endpoint.

After researching several devices, engineers chose the WetSpec200 NIR inline multichannel wet process analysis system manufactured by CI-Semi, a division of CI-Systems. This analyzer measures the absorption spectrum of a fluid sample inline in an optical flow cell that is connected by optical fibers to the analyzer (Fig. 2). These fibers—which may be up to 200 meters long—conduct the light to the flow cells. The light is then returned through optical fibers to a grating-based spectrometer. The absorption spectrum is measured with a photo-diode array.

The analyzer and flow cell are designed as an independent system that can be easily integrated into the fab's data collection network, or into the tool's closed-loop control system. The system is self contained and does not require a separate computer for operation. The spectrometer has automatic internal calibration, enabling excellent stability and repeatability.

Chemical concentration is derived from changes in the NIR

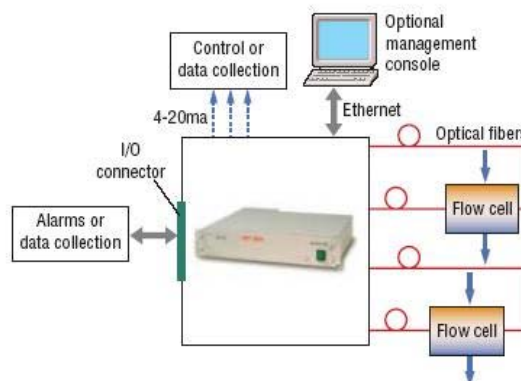


Figure 2. NIR inline concentration analyzer block diagram.

spectrum through a software approach called “chemometrics” (Fig. 3). After “training” the software with a series of measurements of known concentrations, an algorithm correlates the spectral data to changes in concentration to create a “calibration model,” which is then used for determining the concentrations of unknown solutions on-line.

Field installations have demonstrated that models can be developed for most cleaning and etching solutions, including water based solutions such as dilute acids (i.e., SC1, SC2, DSP) and  $H_2O_2$  in slurries, as well as solvent-based chemistries.

A proprietary fiber optic multiplexer allows for the use of up to eight flow cells, improving the cost efficiency of the instrument. In each flow cell, the concentration of several chemicals can be measured simultaneously, and different chemistries can be measured as well. Calibration models are stored inside the instrument, and may easily be changed using the graphical user interface.

### HF concentration application

The NIR inline analyzer was tested in a multiple-use HF bath, with data taken over a 3-month period. The flow cell was mounted in the



filter vent line, which returns the fluid to the outer weir of the bath. This allows for in situ analysis of the actual chemical being used.

Inline data were collected by the analyzer and compared to baselines for multiple ratios of HF to water. Figure 4 shows temperature and percentage HF data from the NIR inline analyzer in real-time. Drops in the temperature and concentration on the graph indicate periodic chemical exchanges.

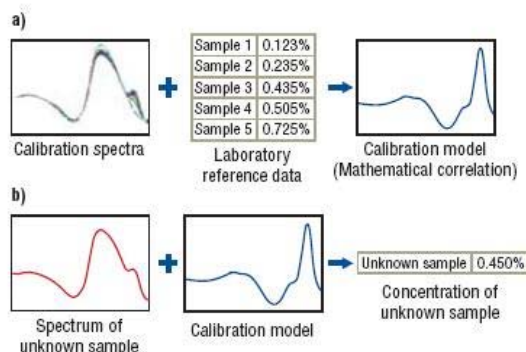


Figure 3. Principles of chemometrics: a) calibration phase and b) measurement phase.

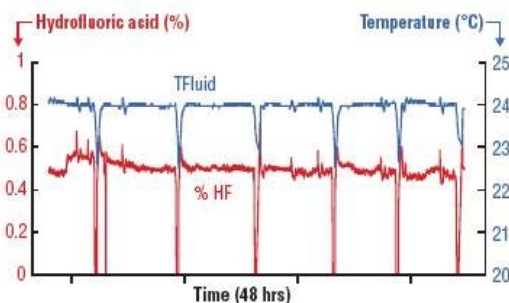


Figure 4. NIR inline analyzer data for HF in water, with periodic chemical changes seen as drops in temperature and concentration.

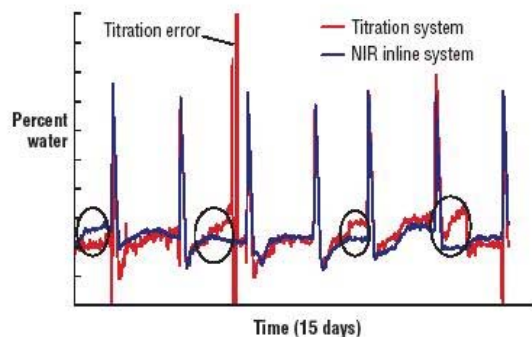


Figure 5. Water concentration in a solvent as measured by the NIR inline analysis system and a titration system, where the circled regions represent regular titration errors in addition to the spike error identified.

### Water concentration in solvent application

For solvent analysis, the NIR inline analyzer was tested head-to-head with a traditional titration system. Each system collected data over a 30-day period. The NIR inline system was installed via the 0.25-in. stainless steel line used by the titration system.

Test results confirm the new system's ability to match the physical titration sampling data, with excellent correlation. The inline analyzer provided real-time data while the titration system provided readings every 1800 sec, due to sampling speeds.

Figure 5 shows that the NIR inline data appear to be more stable than those from the titrator. The circled regions indicate points in which the titration system behaved in an unreasonable manner. The titration system repeatedly produced elevated readings during different timeframes for up to 24 hrs. The elevated readings then dropped unrealistically between samples to match the NIR inline data. The NIR inline system tracked well throughout the experiment and provided more reasonable data.

### Conclusion

Measuring chemical concentrations using multiplexed NIR fixed-grating spectroscopy has many advantages over common methods. It is inline, real time, and accurate, equaling or exceeding the accuracy of chemical titration; unlike conductivity, it allows measurement of multiple-component solutions. Unlike titration, it gives continuous readings in real-time, allowing use in closed-loop control systems. It allows a much faster response time and is not susceptible to bubbles. It offers a more stable and reliable measurement compared to clip-on devices and gives better accuracy at higher speed. The software can be customized to measure different chemistries on different equipment.

For HF-water analysis, the system ensures that the correct acid concentration is in the bath while production wafers are being processed. The system increases productivity by enabling more accurate troubleshooting of bath mix problems. It will reduce the operating costs of running frequent monitor wafer qualifications.

For solvent-water analysis, the system increases productivity by reducing and eliminating scheduled maintenance procedures. The system will reduce operating cost of the water concentration analysis by eliminating reagent solvents and parts. Its greater accuracy assists in reducing scrap risk due to corrosion from high water content. ■

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