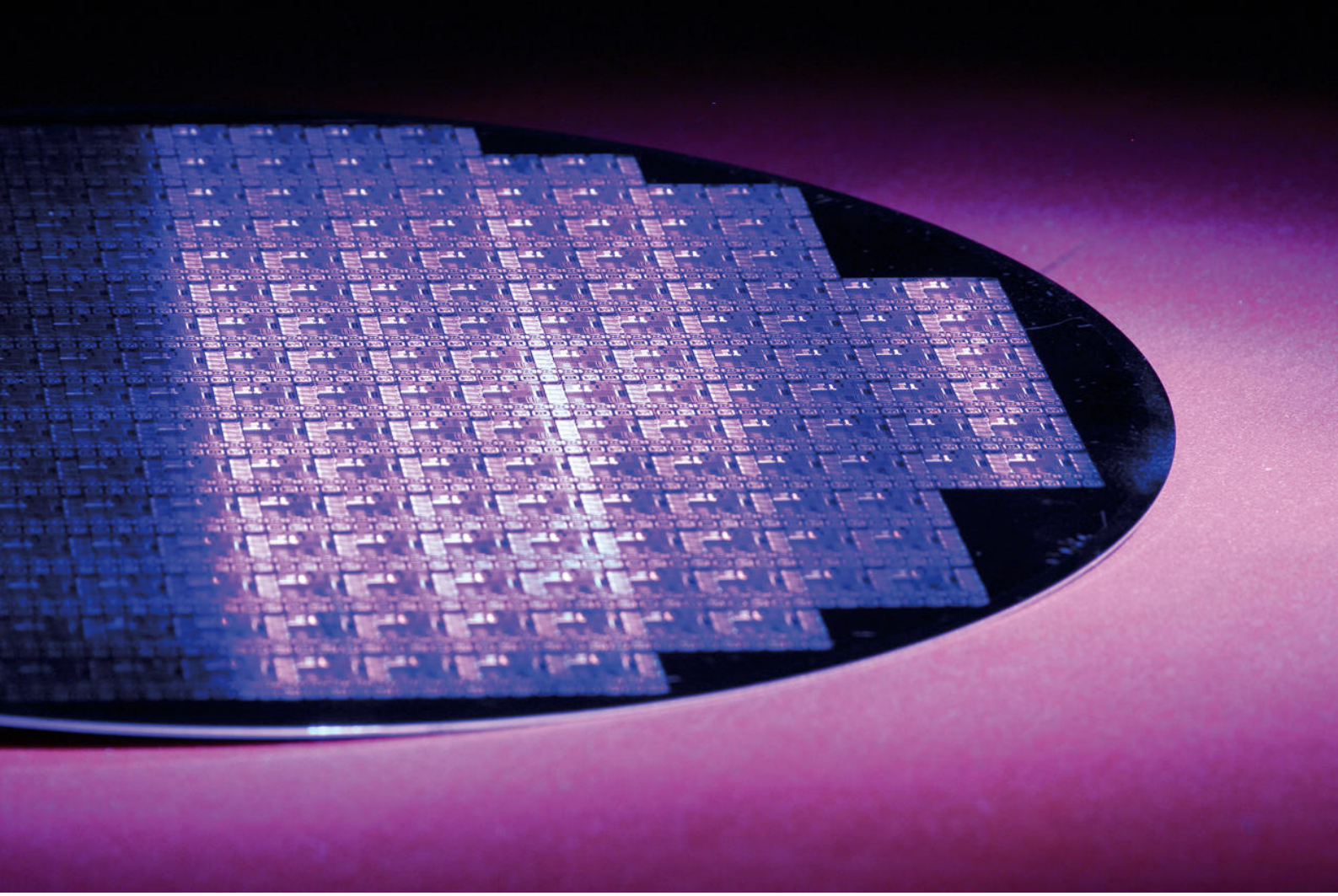

Application Note AN-PAN-1055

Monitoring quality parameters in standard cleaning baths

Measure ammonium hydroxide, hydrogen peroxide, and hydrochloric acid simultaneously with inline NIRS analysis

Silicon semiconductor devices are manufactured on highly polished wafers. Scratches and other imperfections on the wafer could affect the performance of the final product. Therefore, surface preparation is a key step to obtain clean, mirror polished, undamaged silicon surfaces.

Chemical cleaning is a proven method used here to remove contaminants from the wafer surface. The most common process, «RCA clean», cleans wafers via two consecutive standard solutions. The standard cleaning 1 «SC1» bath (or ammonia peroxide- mixture «APM») is composed of NH_4OH and H_2O_2. The standard cleaning 2 «SC2» bath is made of HCl and H_2O_2. The key factors for efficient wafer cleaning are bath residence time and optimum chemical concentration in the cleaning baths. Using near-infrared spectroscopy to monitor the major SC1/SC2 bath constituents inline guarantees increased wafer yields while decreasing defect density.

INTRODUCTION

Efficient silicon wafer cleaning requires optimal process control to ensure an increase in product throughput without additional defects, while increasing production rates and profitability at the same time.

The SC1 bath removes particles, films, and organic residue from the wafer, and forms a thin oxide layer on the surface. However, transition metal hydroxides may also remain on the wafer surface. That is when the SC2 bath becomes essential in the post-chemical mechanical planarization «CMP» cleaning sequence.

SC2 baths are acidic, helping to remove surface alkali and transition metals. This cleaning process leaves a thin passivation layer on the surface of the wafer to avoid future contamination.

The smaller the semiconductor device, the more difficult it is to remove the small particles from the surface of the silicon wafer. Therefore, semiconductor manufacturers perform the standard cleaning steps in a wet bench inside a cleanroom to control the environment and avoid further contamination. This setup leaves very limited space to install an analysis system. Additionally, any chemical handling should be avoided inside the cleanroom area to increase personal and production safety, and to avoid contamination of the wafers.

A safer, more efficient, and faster way to monitor multiple parameters simultaneously in standard cleaning baths is via inline analysis with reagent-free near-infrared spectroscopy (NIRS), as shown in Figure 1.

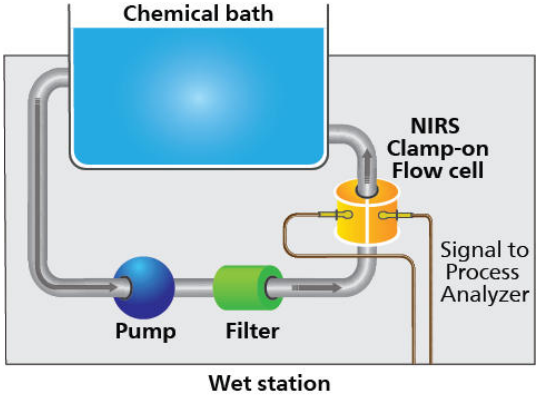

Figure 1. Inline near-infrared spectroscopy (NIRS) system configuration for cleaning bath analysis.

The 2060 *The* NIR-R Analyzer by Metrohm Process Analytics (Figure 2) enables comparison of «real-time» spectral data from the process to a reference method (e.g., titration, HPLC, IC) to create a simple, yet indispensable calibration model for the standard clean baths.

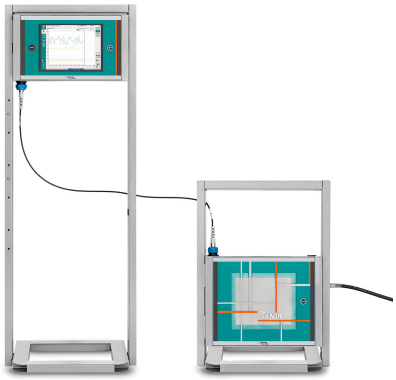

Figure 2. 2060 The NIR-R Analyzer with fiber optic cable and probe.

APPLICATION

Wavelength range used: 800–1300 nm. Reference method: ion chromatography.

When cleanroom space is limited, the NIR cabinet from the 2060 *The* NIR-R Analyzer can be mounted outside the cleanroom in the subfab core facility or simply beneath the wet bench embedded in the processing unit/tool itself. The distance between the instrument and the sample points (up to five possible with one NIR cabinet) can be hundreds of meters apart and simply interfaced to the instrument with low-dispersion optical fibers.

All process baths have a circulation loop made of PFA tubing. The flow cell, designed and customized by Metrohm Process Analytics, can be clamped on to these tubes for easy installation, so there is no need to modify the existing setup (Figure 1). Just clamp the flow cell on and start measuring.

RESULTS

Figure 3 illustrates a trend chart obtained through NIRS for a standard clean 1 (SC1) bath containing ammonia (NH_3) and hydrogen peroxide (H_2O_2). Bath changes are triggered based on predefined concentration or time limits, highlighting the significance of monitoring both parameters. Continuously monitoring the ammonia and hydrogen peroxide levels is crucial for maintaining the integrity of the cleaning process within specified limits.

In this application, the goal was to monitor NH_3 dosage within the SC1 bath to improve recirculation and ensure fast and uniform mixing. Each NH_3 injection shows a definite peak followed by a small decrease of <0.10 wt% (Figure 3), demonstrating the capacity of NIRS to detect even tiny concentration differences.

Compared to traditional analytical methods, the 2060 *The* NIR-R Analyzer offers significant advantages in terms of precision and frequency of measurements, allowing for continuous monitoring and precise control of the SC1 bath.

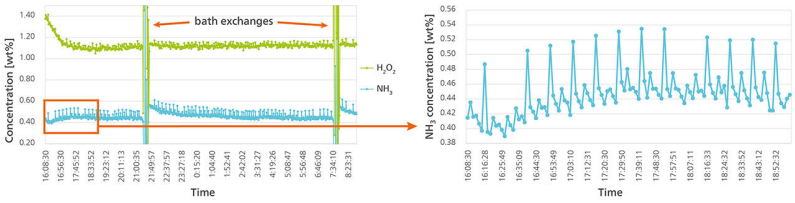

Figure 3. Trend chart of ammonia and hydrogen peroxide concentrations in an SC1 bath. Note the controlled spiking of the baths to maintain concentrations between bath changes.

Table 1. Slurry measurement parameters.

Parameters		Temperature [°C]	Range [wt %]
SC1	NH_4OH	65 ± 3°C	0–1
	H_2O_2	65 ± 3°C	0–2
SC2	HCl	35 ± 3°C	0–1.5
	H_2O_2	35 ± 3°C	0–5
SC2	HCl	RT–70°C	1–5
	H_2O_2	RT–70°C	1–10

REMARKS

An appropriate range of samples covering the process variation is needed to build a calibration model. These samples will be analyzed via NIRS and via a reference method. The precision of the NIRS data is directly correlated to the precision of the reference method. Other process applications are available for the semiconductor industry like: copper, sulfuric acid, and chloride in acid copper baths, acidity in mixed acid etchants, and hydrofluoric acid etch, ammonium hydroxide, and hydrochloric acid in standard clean baths.

CONCLUSION

NIRS analysis enables the comparison of «real-time» spectral data from the process to a primary method (e.g., titration, Karl Fischer titration, HPLC, IC) to create a simple, yet indispensable model for process requirements. Improve semiconductor production control with the Metrohm Process Analytics 2060 *The* NIR-R Analyzer. This process analyzer can monitor up to five process points per NIR cabinet using the multiplexer option.

RELATED PROCESS APPLICATION NOTES

AN-PAN-1012 Online analysis of nickel ion and hypophosphite content in electroless nickel plating baths

AN-PAN-1028 Monitoring tetramethylammonium hydroxide (TMAH) in developer online

AN-PAN-1054 Online monitoring of hydrogen peroxide during the CMP process

BENEFITS FOR NIR SPECTROSCOPY IN PROCESS

- Increased product throughput, reproducibility, production rates, and profitability (less wafer discarding).
- Efficient wafer cleaning by constantly monitoring the standard cleaning baths.
- More savings per measurement point, making results more cost-efficient.
- Safer production due to «real-time» monitoring and no exposure of operators to chemical reagents.

CONTACT

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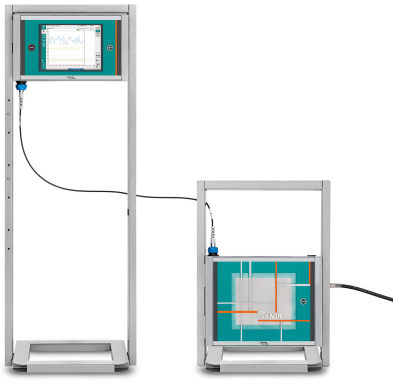
CONFIGURATION



2060 The NIR-R Analyzer

The 2060 *The* NIR-R Analyzer is the next generation of process spectroscopy instruments from Metrohm Process Analytics. With its unique and proven design from the inside out, it delivers accurate results every *10 seconds*. It can provide non-destructive analysis of liquids and solids directly in the process line or in a reaction vessel by using fiber optics and contact probes. It has been designed to connect up to five (5) probes and/or flow-cells. All five channels can be configured independently from each other using our versatile embedded proprietary software.

As part of the 2060 Platform, the 2060 *The* NIR-R Analyzer enables the unique separation of the human interface (HI) and NIR cabinet by optical fibers. This remote configuration allows the placement of both cabinets at different locations around the plant depending on customer preference and area classifications. Besides, it is available in three other versions: the 2060 *The* NIR Analyzer, 2060 *The* NIR-Ex Analyzer, and 2060 *The* NIR-REx Analyzer.