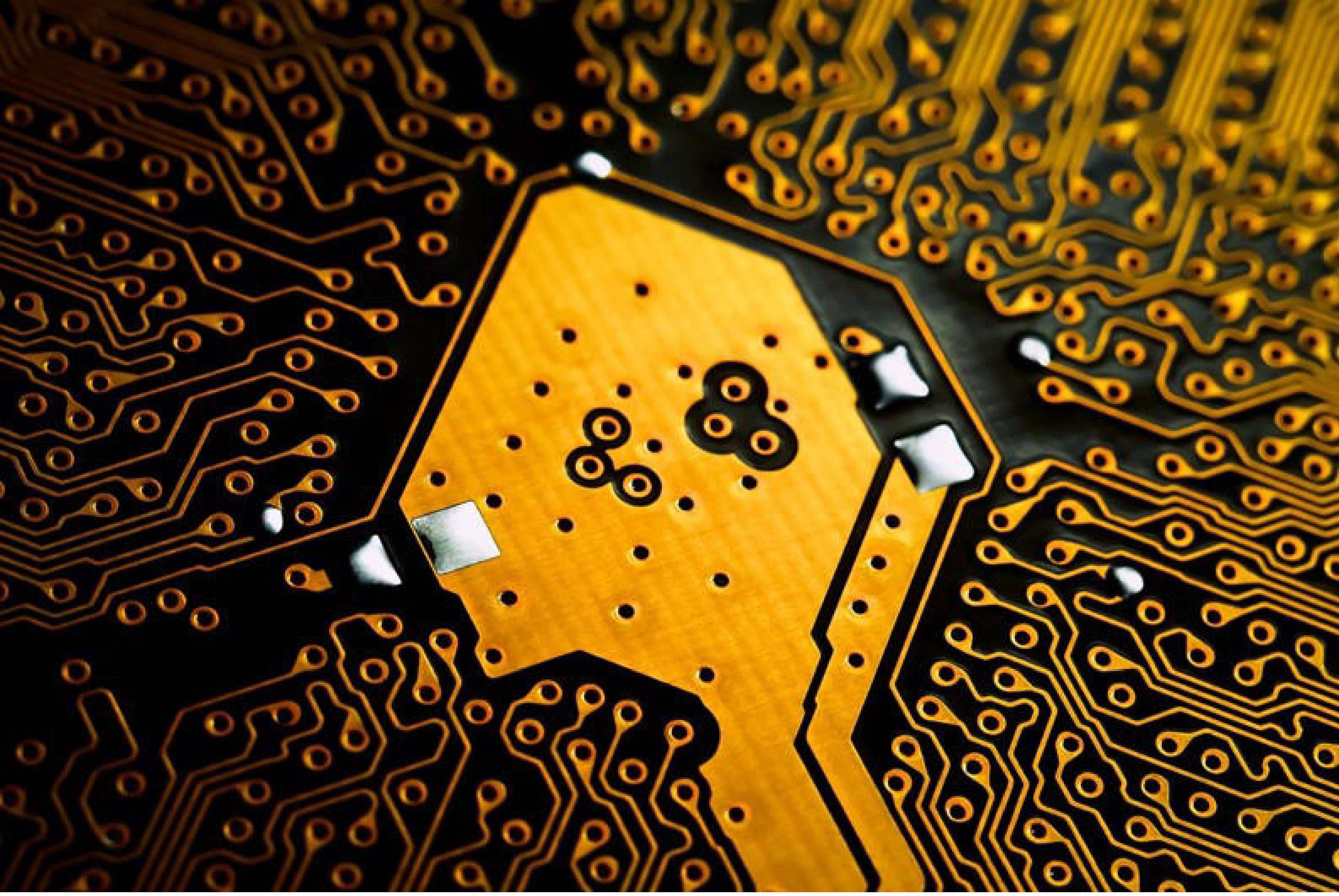


Application Note AN-PAN-1062

Online monitoring of sulfuric acid and hydrogen peroxide using Raman spectroscopy

Etching is used during semiconductor fabrication to chemically remove layers from the surface of the wafer substrate. Etching is a critically important process, and every wafer undergoes multiple etching steps before it is complete. To ensure optimal etching is performed, strict quality control measures must be in place to determine the acid etchant concentration in the varied mixed acid solutions. Depending on the wafer substrate and etching step, SPM (sulfuric acid-peroxide mix, also known as piranha solution), DSP (dilute sulfuric acid-peroxide mix), or DSP+ (dilute sulfuric acid-peroxide-hydrofluoric acid mix) are typically used as etching solutions. Maintaining the correct balance of acid concentrations in these mixtures plays a critical role in optimizing the etch rate, selectivity, and uniformity of the etching process. This Process Application Note presents a method to measure sulfuric acid and hydrogen peroxide online in SPM and DSP solutions simultaneously using Raman spectroscopy with the PTRam Analyzer from Metrohm Process Analytics.

INTRODUCTION

In the semiconductor industry, there are two types of etching processes used: wet and dry etching. Dry etching uses reactive gases (e.g., plasma) to remove the unwanted portions of the semiconductor material. Wet etching is a process that involves the selective removal of material from a substrate by using chemical solutions. These processes are widely used in various industries including electronics, semiconductors, and metalworking.

Wet and dry etching processes are utilized based on the unique requirements of the device being manufactured. However, in semiconductor manufacturing processes, wet etching has been more commonly used than dry etching, particularly for the removal of large amounts of wafer material and the ease of handling [1].

Depending on the material or layer being etched and the intended outcome, several kinds of chemical baths can be utilized for the wet etching of semiconductors. Sulfuric acid-peroxide mix, also known as piranha solution (SPM), and dilute sulfuric acid-peroxide mix (DSP) are typically used to produce silicon wafers [2].

Successful wet etching requires precise control of the reagent concentration in the bath solution. The determination of the acid concentration in mixed acid etching baths is a critical quality control step that can affect the outcome of the etching process.

Both SPM and DSP are potentially toxic solutions that must be handled with extreme caution. When working with these chemicals, personal protective equipment (PPE) should be worn, and all waste materials should be disposed of in accordance with local regulations. This demands online analysis to reduce employee exposure as much as possible and avoid accidents.

Aside from the hazards already mentioned, manual sampling of mixed acid baths is undesirable because of time constraints, potential inaccuracies, and production interruptions. Manual sampling can result in inconsistent sampling depths and locations, potentially providing inaccurate data about the bath's actual condition. To control the process in real time, reduce operational disruptions, enhance safety, and obtain more accurate and representative data, a better solution is necessary.

A safer, more efficient, and faster way to monitor multiple parameters simultaneously in mixed acid baths is via reagent-free online analysis with Raman spectroscopy. The PTRam Analyzer from Metrohm Process Analytics (Figure 1) is an ideal solution for this kind of challenging situation. This Raman analyzer enables the comparison of «real-time» spectral data from the process to a reference method (e.g., titration,

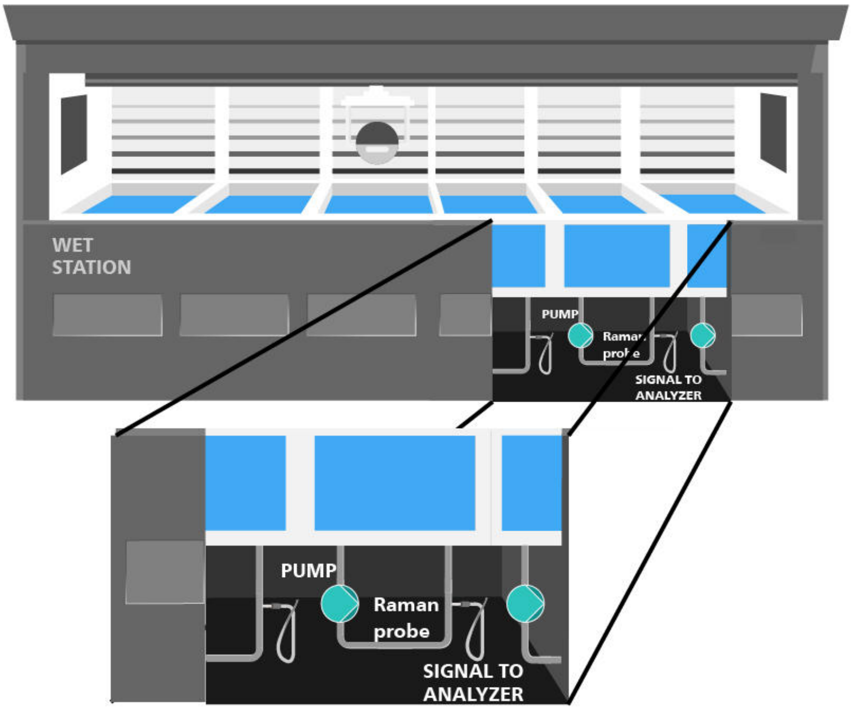
Figure 1. The PTRam Analyzer from Metrohm Process Analytics.

There is minimal space available to install an analysis system within the wet bench area (Figure 2a). Therefore, the PTRam Analyzer is the ideal solution for restricted spaces due to its small dimensions. Thanks to the embedded IMPACT software and the variety of industrial communication protocols, results can be transmitted in the same format to any Distributed Control System (DCS), a Programmable Logic Controller (PLC), or a Supervisory Control And Data Acquisition (SCADA) system for further actions (e.g., to adjust chemical dosing).

APPLICATION

Perfluoroalkoxy (PFA) tubing is a popular choice for applications with aggressive media due to its excellent chemical resistance, which is greatly useful in this application. Moreover, Raman spectroscopy allows the measurement through transparent and semi-transparent materials. This application takes full advantage of this property by having the sample measured through PFA tubing (Figure 2b).

a)


WET
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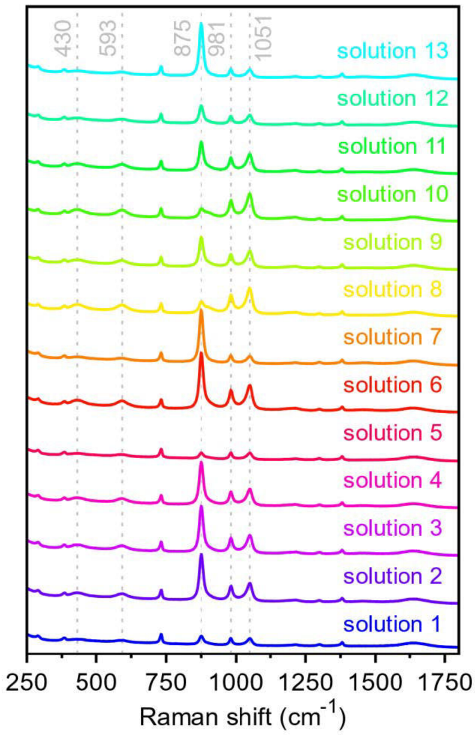

Figure 2. a) Stylization of suggested placement for an online Raman probe on a wet bench in the wafer etching process and b) Raman spectra collected during measurements.

Table 1. Parameters and results of the quantitative method development for sulfuric acid and peroxide with online Raman spectroscopy.

	H_2SO_4	H_2O_2
Concentration [%]	6.2–12	4.6–10
Wavelength range [cm^{-1}]	350–1200	250–2500
R^2	0.9991	0.9993
SEC [%]	0.0657	0.0579
SECV [%]	0.1383	0.0882

CONCLUSION

The use of Raman spectroscopy, specifically the PTRam Analyzer from Metrohm Process Analytics, presents a reliable and efficient method for online monitoring of the sulfuric acid and hydrogen peroxide content in etching solutions such as SPM and DSP. This online analysis technique enables real-time measurement of multiple parameters simultaneously, providing precise control over the reagent concentrations in the mixed acid baths. With the ability to compare spectral data to reference methods, Raman spectroscopy can be part of a safer production environment by eliminating operator exposure to hazardous chemical reagents. Additionally, using Raman spectroscopy to monitor the etching bath composition enhances wafer cleaning efficiency and increases product throughput, reproducibility, production rates, and overall profitability by minimizing wastage and ensuring optimal etching processes.

RELATED DOCUMENTS

8.000.5421 PTRam Analyzer - Monitor and optimize your process with Metrohm Process Raman Analyzers

AN-PAN-1055 Monitoring quality parameters in standard cleaning baths AN-NIR-090 Quality Control of Mixed Phosphoric, Sulfuric, Nitric, and Hydrofluoric Acids

AN-NIR-090 Quality Control of Mixed Phosphoric, Sulfuric, Nitric, and Hydrofluoric Acids

WP-067 Quality control of semiconductor acid baths as per ASTM E1655 – Time- and cost-efficient with NIRS

BENEFITS FOR RAMAN SPECTROSCOPY IN PROCESS

- Safer production due to «real-time» monitoring and no exposure of operators to chemical reagents (e.g., H_2SO_4).
- Efficient wafer cleaning by constantly monitoring the baths.
- Increased product throughput, reproducibility, production rates, and profitability (less wafer discarding).

REFERENCES

1. *Dry Etching vs. Wet Etching - Differences and Applications*. https://www.xometry.com/resources/blog/dry-etching-vs-wet-etching/ (accessed 2023-05-03).
2. Clews, P. J.; Nelson, G. C.; Matlock, C. A.; et al. Sulfuric Acid/Hydrogen Peroxide Rinsing Study, Sandia National laboratories.

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CONFIGURATION

PTRam Analyzer

The PTRam Analyzer is a process development 785 nm Raman analyzer designed for product and process development use in labs and pilot plants. It is a high performance, precise, robust, and reliable Raman system featuring self-calibration and automated performance validation to ensure validity of every measurement.

This single-sample channel system includes a lab fiber optic probe with an user-replaceable shaft. The PTRam is 19” rack-mountable. The PTRam operates with Vision software and it can be connected with a 2060 Human Interface.