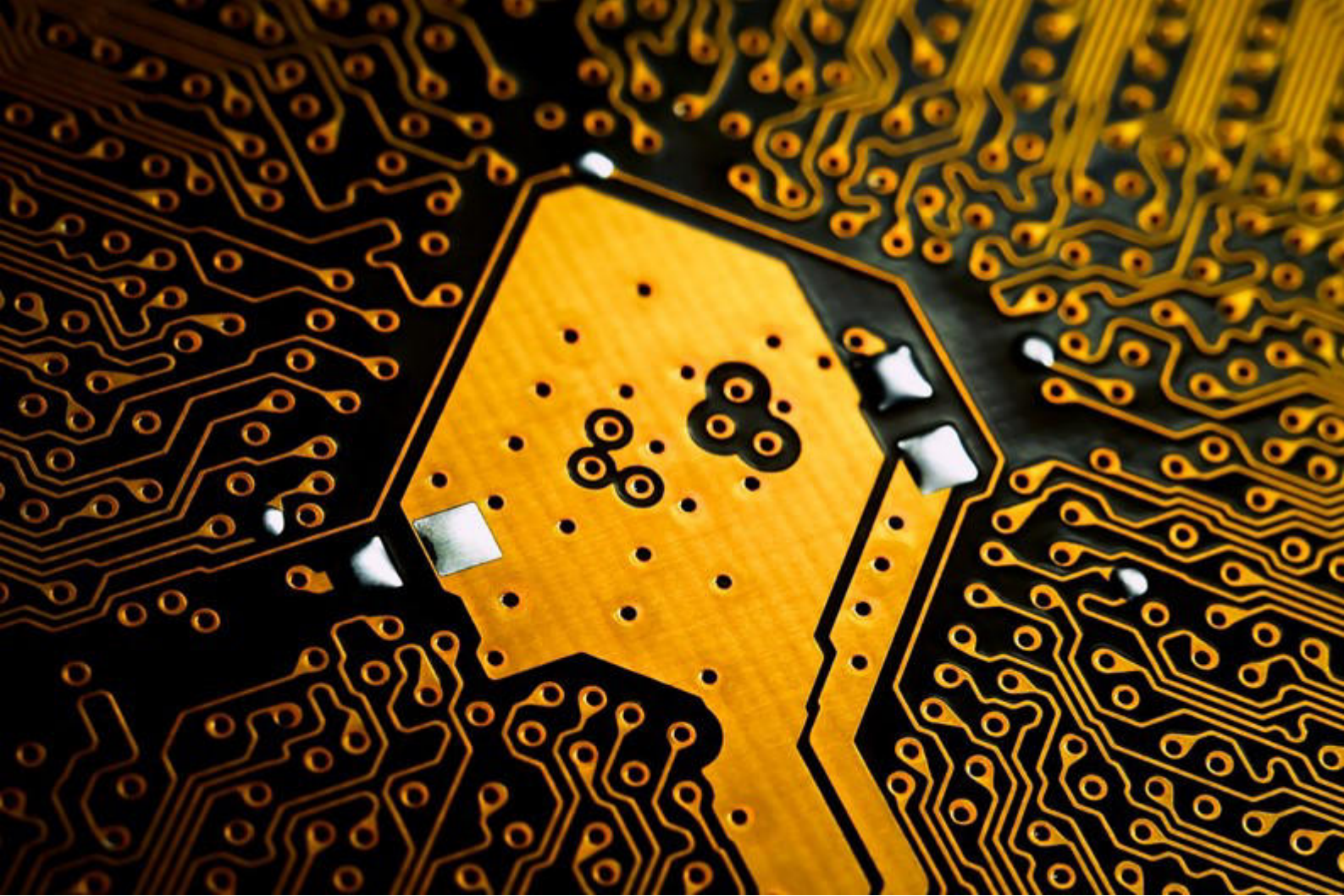




Application Note AN-PAN-1062

# 利用拉曼光谱对硫酸和过氧化氢进行 在线监测

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



**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)



b)



**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 <sub>2</sub> SO <sub>4</sub> | H <sub>2</sub> O <sub>2</sub> |
|--------------------------------------|--------------------------------|-------------------------------|
| Concentration [%]                    | 6.2–12                         | 4.6–10                        |
| Wavelength range [cm <sup>-1</sup> ] | 350–1200                       | 250–2500                      |
| R <sup>2</sup>                       | 0.9991                         | 0.9993                        |
| SEC [%]                              | 0.0657                         | 0.0579                        |
| SECV [%]                             | 0.1383                         | 0.0882                        |

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.,  $\text{H}_2\text{SO}_4$ ).
- **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

PTRam Analyzer为一款 785 nm 进程开发拉曼分析仪,其设计旨在用于分析实验室和试点工厂环境中的产品和进程开发。这是一个高性能、准确、结实且可靠的拉曼系统,其具有自校正和自动性能校验功能,来确保每次测量的有效性。

这一单样本通道系统包括了一个实验室光纤探头,以及用户可更换的框架。该 PTRam 为 19" 可固定样品盘。其 PTRam 可通过 Vision 软件进行操作,并可以与 2060 Human Interface 连接。