

Application Note AN-H-140

磷酸、硝酸和醋酸混合物的滴定

Fast and reliable analysis of phosphoric etchants used in the semiconductor industry by thermometric titration

Aluminum and its alloys are used for wiring in microchips [1]. To selectively wet etch aluminum, an etching bath made of phosphoric acid, nitric acid, and acetic acid (PAN etchant) is used. This acid mixture must be analyzed and monitored for optimal and efficient etching.

The SEMI C37 standard uses potentiometric titration to measure total acidity and phosphoric acid content. However, nitric acid must be analyzed by UV/VIS spectroscopy, while acetic acid content is calculated from the other results [2]. Thermometric titration (TET) is an alternative PAN etchant analysis method which can determine all three acids quickly.

In this Application Note, the acid concentrations are determined in sequence using a single titration. Compared to potentiometric titration, TET is faster and more convenient. On a fully automated system, the complete analysis takes about 95 seconds.

SAMPLE AND SAMPLE PREPARATION

This application is demonstrated on a simulated aqueous etching solution composed of phosphoric acid, acetic acid, and nitric acid. Sample preparation is not required.

EXPERIMENTAL

The determinations are carried out on an OMNIS Professional Titrator equipped with a dThermoprobe (**Figure 1**). To avoid manually handling chemicals, all solutions are automatically added using an OMNIS Dosing Module.

An appropriate amount of sample is pipetted into the titration vessel and deionized water is added. Afterwards, the solution is titrated until after the third exothermic endpoint with standardized sodium hydroxide (**Figure 2**).



Figure 1. OMNIS Titrator Professional equipped with a dThermoprobe and a rod stirrer.

RESULTS

This method offers very accurate results for PAN etchant, as displayed in **Table 1**.

Table 1. Results of the thermometric titration of a mixture containing 10.5% acetic acid, 24.5% phosphoric acid, and 35% nitric acid (n = 3).

Sample (n = 3)	Mean value in %	SD(rel) in %
CH_3COOH (10.5%)	9.82	0.5
H_3PO_4 (24.5%)	25.4	0.7
HNO_3 (35%)	36.1	0.5



Figure 2. Titration curve showing the thermometric determination of a three-acid mixture. The EPs are explained in Table 2.

Table 2. Explanation of TET endpoints from Figure 2.

EP1	EP2	EP3
HNO_3 (fully dissociated)	CH_3COOH (pK_a = 4.75)	–
H_3PO_4 (pK_{a1} = 2.12)	H_3PO_4 (pK_{a2} = 7.21)	H_3PO_4 (pK_{a3} = 12.36)

CONCLUSION

Thermometric titration is a very fast and accurate method that can determine the concentration of acetic, phosphoric, and nitric acids in one titration. This method can differentiate between the three acid components with a determination time of **less than two minutes**. No sensor maintenance is required, making TET a robust alternative to other PAN etchant analysis methods.

REFERENCES

1. *Aluminum technology - Metallization - Semiconductor Technology from A to Z - Halbleiter.org*. https://www.halbleiter.org/en/metallization/aluminum-technology/ (accessed 2023-07-26).
2. *SEMI C37 - Specification for Phosphoric Etchants*; SEMI C37; SEMI: Milpitas, CA, USA, 2011.

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CONFIGURATION



OMNIS Titrator

创新型、模块式电位分析 OMNIS Titrator 滴定仪,适于独立运行或作为 OMNIS 滴定系统的核心元件运行。由于采用 3S 试剂瓶适配器技术,处理化学品很安全。可以使用测量模块和计量管单元自由配置滴定仪,并在需要时扩展一台搅拌器。由于采用不同的软件功能许可证,因此可以有不同的测量模式和功能。

- 通过计算机或本地网络控制
- 可以为其他应用或辅助溶液另外连接四个滴定模块或加液模块
- 螺旋搅拌器的连接方式
- 可提供不同大小的计量管:5、10、20 或 50 mL
- 采用 3S 技术的试剂瓶适配器:安全处理化学品,自动传输生产商的原始试剂数据

测量模式和软件选项:

- 终点设定滴定:“Basic” 功能许可证
- 终点和等当点滴定(单一/动态):“Advanced” 功能许可证
- 终点和等当点滴定(单一/动态),包括平行滴定:“Professional” 功能许可证



dThermoprobe

高灵敏性数字温度探针,用于使用 OMNIS 进行热滴定。

Thermoprobe 温度电极具有较短的响应时间和较高的分辨率,能够精确检测温度变化。

该传感器可以用于不含 HF 的水溶液和非水溶液,例如,测定:

- 酸值 (TAN) 根据 ASTM D8045
- 基数 (TBN)
- 游离脂肪酸
- Ca/Mg 测定
- 磷酸盐



OMNIS 10 mL

智能 10 mL 计量管单元,用于一台 OMNIS Titrator、滴定模块或加液模块。该计量管单元特别推荐用于以下溶液:

- 水性碱溶液
- 滴定剂 5
- 硝酸银溶液
- 非水性碱溶液
- 高锰酸盐溶液
- EDTA 溶液

包含加液软管和防扩散滴管头。

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- 温度等当点滴定 (TET)
- MEAS U / T / pH
- 灵快量化液体处理
- 仅使用一个 OMNIS Tritator 的内部滴定管进行滴定