



Application Note AN-H-140

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 ₃ COOH (10.5%)	9.82	0.5
H ₃ PO ₄ (24.5%)	25.4	0.7
HNO ₃ (35%)	36.1	0.5

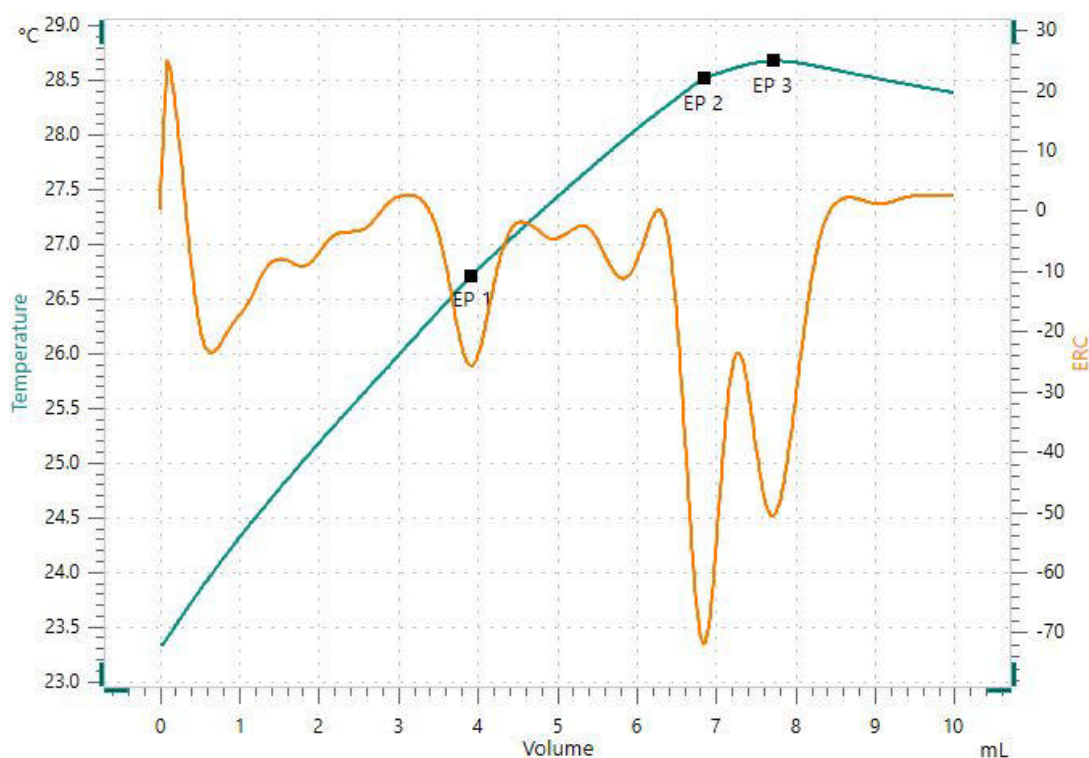


Figure 2. Titration curve showing the thermometric determination of a three-acid mixture. The EPs are explained in Table 2.

Table 2. Explanation of TET endpoints from Figure 2.

EP1	EP2	EP3
HNO ₃ (fully dissociated)	CH ₃ COOH (pK _a = 4.75)	–
H ₃ PO ₄ (pK _{a1} = 2.12)	H ₃ PO ₄ (pK _{a2} = 7.21)	H ₃ PO 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

新型、模式位分析 OMNIS Titrator 滴定,于独立行或作 OMNIS 滴定系的核心元件行。由于采用 3S 瓶配器技,理化学品很安全。可以使用量模和量管元自由配置滴定,并在需要展一台拌器。由于采用不同的件功能可,因此可以有不同的量模式和功能。

- 通算机或本地网控制
- 可以其他用或助溶液外接四个滴定模或加液模
- 螺旋拌器的接方式
- 可提供不同大小的量管:5、10、20 或 50 mL
- 采用 3S 技的瓶配器:安全理化学品,自生商的原
始数据

量模式和件:

- 点定滴定:“Basic” 功能可
- 点和等当点滴定(一/):“Advanced” 功能可
- 点和等当点滴定(一/),包括平行滴定
:“Professional” 功能可



dThermoprobe

高敏性数字温度探,用于使用 OMNIS 行滴定。

Thermoprobe 温度具有短的和高的分辨率,能精温度化。

感器可以用于不含 HF 的水溶液和非水溶液,例如,定:

- 酸 (TAN) 根据 ASTM D8045
- 基数 (TBN)
- 游脂肪酸
- Ca/Mg 定
- 酸



OMNIS 10 mL

智能型量管元 10 mL,用于 OMNIS Titrator、Titration Module 或 Dosing Module。量管元推荐用于以下溶液:

- 水性溶液
- 滴定 5
- 硝酸溶液
- 非水性溶液
- 高酸溶液
- EDTA 溶液

包括量管和防散滴管。

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- 温度等当点滴定 (TET)
- MEAS U / T / pH
- 用 OMNIS Tritator 的内部滴定管行滴定