Application Note AN-H-140

Titration of phosphoric, nitric, and acetic acid mixtures

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

Aluminum is used for wiring layers in semiconductors [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. Hilleringmann, U. *Silicon Semiconductor Technology: Processing and Integration of Microelectronic Devices*; Springer Fachmedien: Wiesbaden, 2023. https://doi.org/10.1007/978-3-658-41041-4.
2. *SEMI C37 - Specification for Phosphoric Etchants*; SEMI C37; SEMI: Milpitas, CA, USA, 2011.

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CONFIGURATION

OMNIS Titrator with magnetic stirrer, without function license

Innovative, modular potentiometric OMNIS Titrator for stand-alone operation or as the core of an OMNIS titration system. Thanks to 3S Liquid Adapter technology, handling chemicals is more secure than ever before. The titrator can be freely configured with measuring modules and cylinder units and can have a stirrer added as needed. Thanks to various software function licenses, various measuring modes and functionalities are possible.

- Control via PC or local network
- Connection option for up to four additional titration or dosing modules for additional applications or auxiliary solutions
- Connection option for one rod stirrer
- Various cylinder sizes available: 5, 10, 20 or 50 mL
- Liquid Adapter with 3S technology: Secure handling of chemicals, automatic transfer of the original reagent data of the manufacturer

Measuring modes and software options:

- Endpoint titration: "Basic" function license
- Endpoint and equivalence point titration (monotonic/dynamic): "Advanced" function license
- Endpoint and equivalence point titration (monotonic/dynamic) with parallel titration: "Professional" function license

dThermoprobe

High-sensitivity digital temperature sensor for thermometric titration with OMNIS.

The Thermoprobe has a short response time and a high resolution, which enables precise recording of even the smallest temperature changes.

This sensor can be used in aqueous and nonaqueous solutions which do not contain any HF, for determinations such as:

- Acid number (TAN) in accordance with ASTM D8045
- Total base number (TBN)
- Free fatty acids
- Ca/Mg determination
- Phosphate

Cylinder unit OMNIS special, 10 mL

Intelligent 10 mL cylinder unit for one OMNIS Titrator, Titration Module or Dosing Module. This cylinder unit is especially recommended for the following solutions:

- Aqueous alkaline solutions
- Titrant 5
- Silver nitrate solutions
- Nonaqueous alkaline solutions
- Permanganate solutions
- EDTA solutions

Includes dosing tubing and antidiffusion tip.

OMNIS

A WHOLE NEW LEVEL OF PERFORMANCE

Function license Thermometric Titrator

Function license "Thermometric Titrator" for the OMNIS Titrator

Contains the function modes

- Thermometric Titration (TET)
- MEAS U/T/pH
- Liquid Handling
- Titration only with internal buret of an OMNIS Titrator