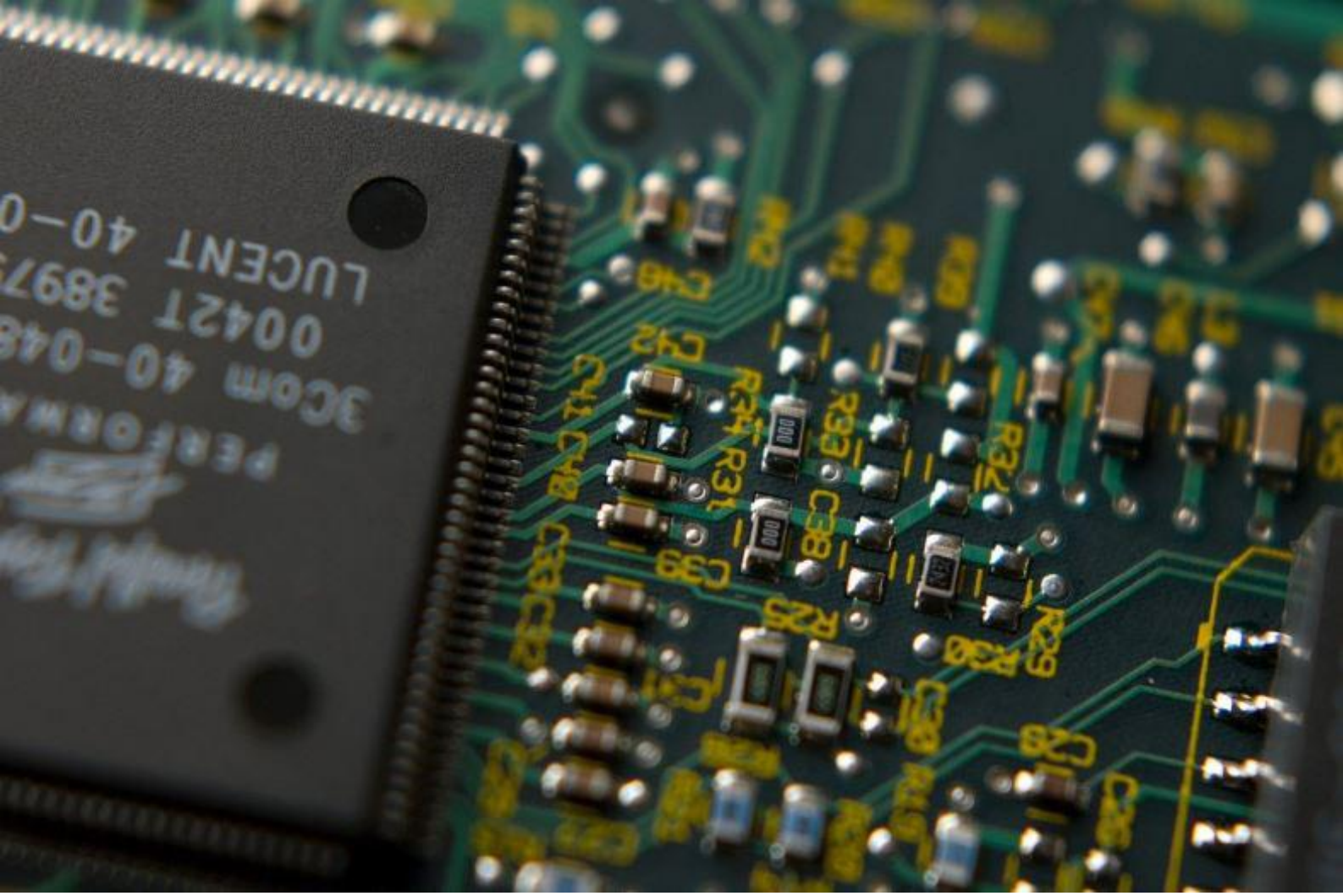

Application Note AN-PAN-1028

Monitoring tetramethylammonium hydroxide (TMAH) in developer online

Tetramethylammonium hydroxide (TMAH) is a quaternary amonium salt mostly used in the production of integrated circuits (IC), printed circuit boards (PCB), and flat panel displays (LCD), and photolithography is the most common process used to manufacture these devices.

In this process, a photoresist developer is used to transfer a pattern on a substrate. The chemicals used in the semiconductor industry must be exceptionally pure because even traces of contaminants have a negative effect on electrical properties.

The development stage is a critical step in photolithography, and in order to be successful, this process must be optimized in order to increase production efficiency. This Process Application Note presents a method to monitor the TMAH concentration in the developer solution via online process titration. This is a multiparameter analytical technique that can accurately monitor TMAH using a combined pH electrode.

INTRODUCTION

For the production of semiconductors it is of the utmost importance to use extremely high purity chemicals. The presence of impurities (even trace concentrations) can significantly affect the material's electrical properties. The same applies for the concentrations of the chemicals used during the production process. In back end of line (BEOL) processing, the photolithography process uses light to print thin film patterns from a photomask (an opaque plate with openings for light) on a micrometer (or smaller) scale with a light-sensitive photoresist chemical applied thinly on the silicon wafer.

After a certain exposure time, the printed circuit is developed and the photoresist can be stripped away in preparation for the next steps (Figure 1). Tetramethylammonium hydroxide (TMAH, $N(CH_3)_4OH$) is an alkaline ingredient in photoresist developer kept at a concentration between 2.38–2.62% in many applications (Figure 2). TMAH is highly effective in stripping off the acidic photoresist as it becomes soluble in the developer. TMAH-based photoresist developers have replaced many traditional developers (such as KOH and NaOH) since these processes increasingly need to be metal-ion-free.

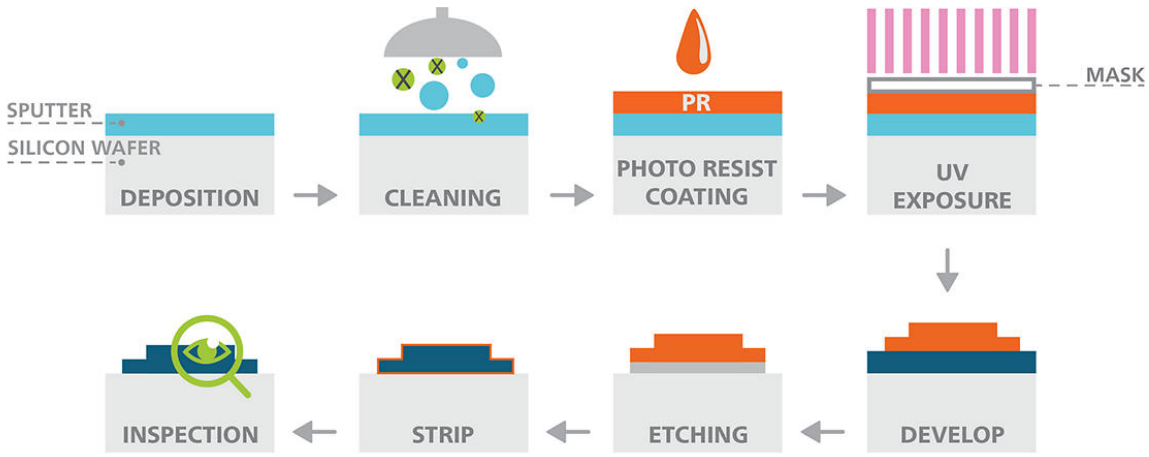

Figure 1. Diagram of the photolithography process in integrated circuit production.

A concentrated solution of TMAH (25%) is diluted in the Chemical Central Supply System (CCSS) and the appropriate percentage is then added to the production line. Used TMAH developer containing the photoresist residue is returned and more TMAH is added to adjust the concentration. Once the amount of residue has reached a certain level, the waste is removed. A purification unit can be used to minimize TMAH in the waste stream.

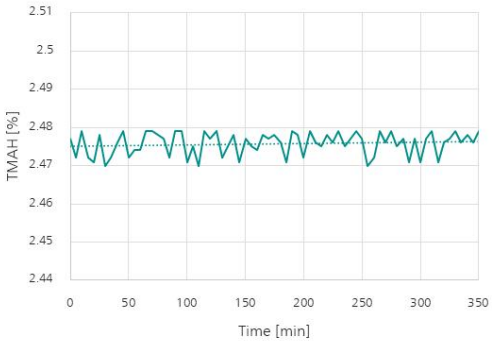

Figure 2. Example trend chart for TMAH (%) coming from the CCSS.

Development is a critical step, and the 2035 Process Analyzer - Potentiometric from Metrohm Process Analytics (Figure 3) can monitor and even stabilize the TMAH concentration in the developer solution, ensuring proper photoresist stripping while minimizing the exposure of personnel to highly toxic TMAH, thus providing a complete turnkey solution. Continuous online analysis is also critical for the batch release of a chemical blending/dilution system for diluted TMAH.

APPLICATION

The 2035 Process Analyzer configured for potentiometric titration performs the accurate analysis of TMAH online using a combined pH electrode. Precise dosing of TMAH in the developer solution by the analyzer is also a possibility to ensure a stable concentration for every batch.

Figure 3. 2035 Process Analyzer - Potentiometric for accurate determination of TMAH in developer.

TYPICAL RANGES

Diluted tetramethylammonium hydroxide (TMAH):	2.38–2.62%, as concentrate: 25%

FURTHER READING

Related application notes

AN-PAN-1054 Online monitoring of hydrogen peroxide during the CMP process

AN-PAN-1055 Monitoring quality parameters in standard cleaning baths

Other related documents

Semiconductor industry – Reliable online, inline and atline solutions for your process requirements

REMARKS

Other applications are available for the semiconductor industry including:

- copper, sulfuric acid, and chloride in acid copper baths
- hydrogen peroxide in CMP slurry
- acidity in mixed acid etchants
- hydrofluoric acid, ammonium hydroxide, and hydrochloric acid in standard clean baths

BENEFITS FOR TITRATION IN PROCESS

- **Enhanced printed circuit yields** with qualified TMAH compositions
- **Increased product throughput** with less wafer defects
- **Greater mixing integrity and purity** in the CCSS
- **Enhanced** reproducibility, production rates, and profitability (less waste)

CONTACT

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CONFIGURATION

2035 Process Analyzer - Potentiometric

The 2035 Process Analyzer for Potentiometric Titration and Ion-Selective Measurements performs analyses with dedicated electrodes and titrants. Additionally, this version of the 2035 Process Analyzer is also suitable for Ion-Selective Analysis using Metrohm high performance electrodes. This accurate standard addition technique is ideal for more difficult sample matrices.

The potentiometric version of the analyzer offers the most accurate results of all measuring techniques available on the market. With far more than 1000 applications already available, titration is also one of the most used methods for analysis in almost any industry for hundreds of components varying from acid/base analysis to metal concentrations in plating baths.

Titration is one of the most widespread absolute chemical methods in use today. The technique is straightforward with no need for calibration.

Some titration options available for this configuration:

- Potentiometric titration
- Colorimetric titration with Fiber Optic Technology
- Moisture determination based on the Karl Fischer titration method