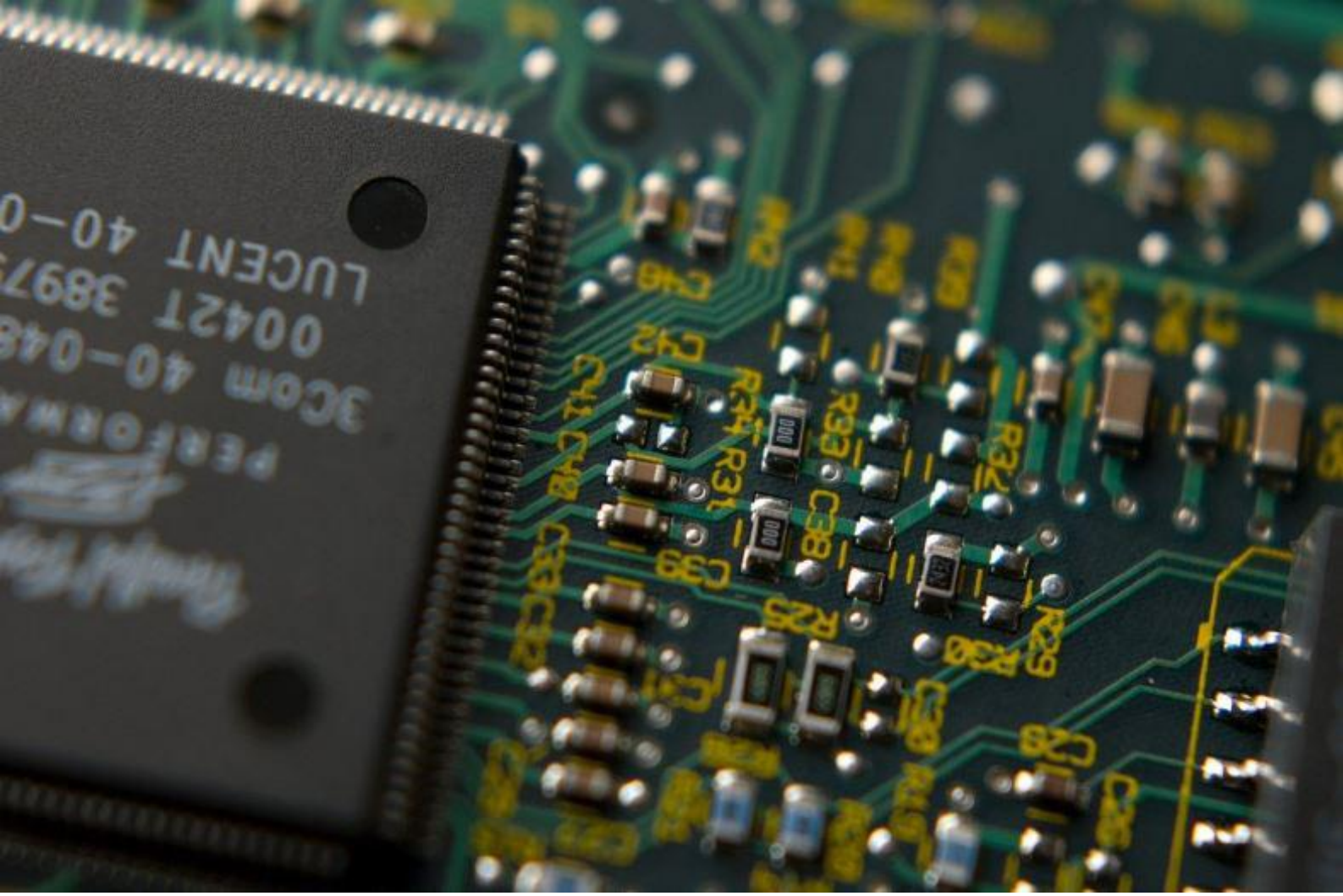

Application Note AN-PAN-1028

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.

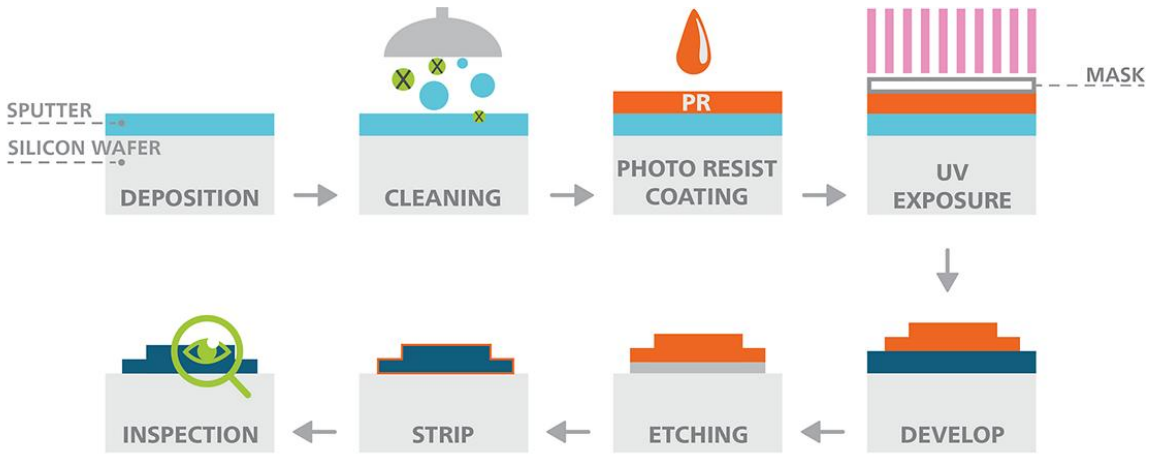

Figure 1. Diagram of the photolithography process in integrated circuit production.

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.

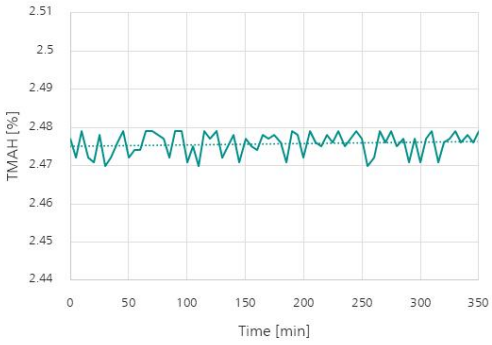

Figure 2. Example trend chart for TMAH (%) coming from the CCSS.

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

Metrohm France
13, avenue du Québec - CS 90038
91978 VILLEBON COURTABOEUF CEDEX
info@metrohm.fr

CONFIGURATION

2035 Process Analyzer – Potentiométrie

Le 2035 Process Analyzer pour titrage potentiométrique et mesures sélectives d'ions réalise des analyses avec des électrodes et des titrants dédiés. De plus, cette version du 2035 Process Analyzer convient également à l'analyse sélective d'ions à l'aide d'électrodes haute performance de Metrohm. Cette technique précise d'addition standard est idéale pour des matrices d'échantillons qui s'avèrent plus difficiles.

La version potentiométrique de l'appareil d'analyse délivre des résultats plus précis que toutes les techniques de mesure disponibles sur le marché. Avec largement plus de 1 000 applications déjà disponibles, le titrage est l'une des méthodes les plus utilisées dans pratiquement tous les secteurs industriels pour l'analyse de centaines de composants qui varient de l'analyse acide/base aux concentrations de métaux dans les bains galvaniques. Le titrage est l'une des méthodes chimiques absolues les plus répandues en usage aujourd'hui. Cette technique est directe et ne requiert aucun calibrage.

Quelques options de titrage disponibles pour cette configuration :

- Titrage potentiométrique
- Titrage colorimétrique avec la technologie à fibre optique
- Détermination de l'humidité basée sur la méthode de titrage Karl Fischer