Metrologies of Amine and Ammonium in Post Etch Residue Removal

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Introduction

Post Etch Residue Removal (PERR) Challenges in the semiconductor industry driven to sub-10 nm node

- Removing residues completely from vias and metal lines with diminished feature sizes and increasing number of interconnect layers
- Not corroding metals or affecting low-κ dimensions and properties

Most modern PERR formulations include multiple subcomponents for various purposes such as corrosion inhibitors and chelators, while ammonium and amines remain the most common and basic active ingredients. The monitoring and control of these species become challenging because traditional metrologies may not be satisfactory due to the complexity of the solution.

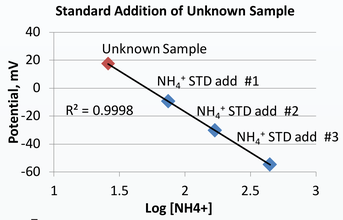
Metrology of Ammonium for online Process Control

Method	Typical Spec	Pros	Cons
NIR	3% acc., 1% RSD	Real time analysis (<1 min) non-contact	Method establishment requires set of "learning" Standards and can be limited by wide pH range.
Electrochemical	5% acc., 3% RSD	Fast (<5 min) Minimal interference Low cost	May require chemical use (buffer)
Reagent Photo-metric	3% acc., 1% RSD	No need for full Standard	Requires multiple reagents Certain amines can interfere
IC	3% acc., 1% RSD	Free matrix interference	High cost >15 min analysis time

• Measuring Ammonium by Electrochemical Method

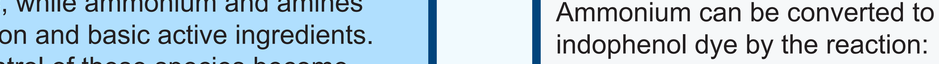
Ammonium can be measured by Ion Selective Electrode (ISE) method. Under ideal conditions, the potential (E) of an ISE is given by the Nernst equation:

$$E = E_0 - (2.303\frac{RT}{nF})\ \log[NH_4^+]$$



• Measuring Ammonium by Photometric Method

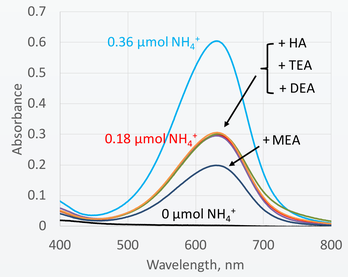
Ammonium can be converted to indophenol dye by the reaction:



Potential interference Test:

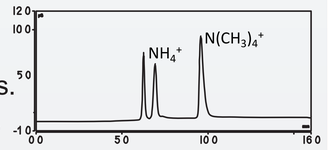
- ○ Hydroxylamine (HA)
- ○ Monoethanolamine (MEA)
- ○ Diethanolamine (DEA)
- ○ Triethanolamine (TEA)

Note: 0.18 µmol amines spiked into 0.18 µmol of NH_4^+



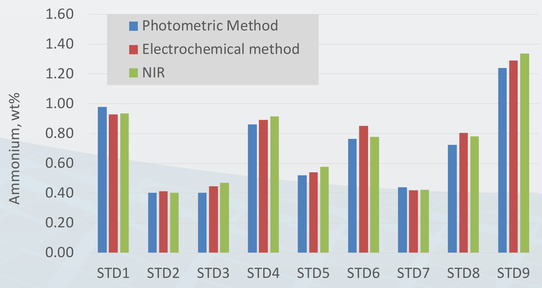
• Measuring Ammonium by IC

Ammonium can be be analyzed by ion chromatography, free from potential interferences of foreign ions.



• Method Comparison of Ammonium Analysis in PERR Samples

Ammoniums in PERR samples were measured by photometric, electrochemical, and NIR methods. The results obtained by the three methods are highly comparable.



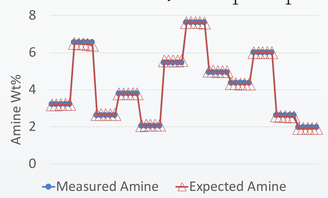
Metrology of Amines for Online Process Control

Method	Typical Spec	Pros	Cons
NIR	3% acc., 1% RSD	Real time analysis (<1 min) non-contact	Method establishment requires set of "learning" Standards
Acid Base Titration	3% acc., 2% RSD	No need for full Standard Low cost	Requires chemical use (reagents and titrants) Potential interference from bases with similar pKa as the analyte amine

• Measuring Amine by NIR

Amines can be measured by Near-infrared (NIR) spectroscopy combined with multivariate calibration.

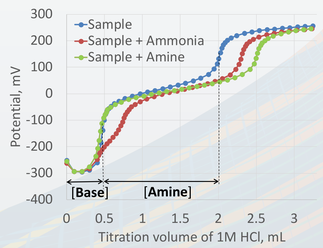
$$c_{analyte} = c_{\lambda_1} \times A_{\lambda_1} + \ldots c_{\lambda_i} \times A_{\lambda_i} + \ldots c_{\lambda_n} \times A_{\lambda_n} + c_0$$



Samples	Expected Amine wt%	Measured Amine wt%	Relative Error
STD3	2.61	2.65	1.55%
STD3+Ammmonia	2.59	2.55	2.47%
STD5	2.03	2.08	0.00%
STD5+TMAH	1.97	1.91	-1.72%
STD6	5.29	5.29	-2.81%
STD6+Solvent	5.14	5.02	-2.45%
STD6+Amine	9.29	9.25	-0.47%
STD6+Chelator	5.25	5.27	0.32%
STD6+DIW	4.80	4.80	-0.14%

• Measuring Amine by Titration

As an organic base, amines can be titrated by acid forming conjugated acids. Direct titration tends to have large errors due to other sources of acids/bases.



The method is developed to avoid interference from the alkalinity of the sample. Common sources of alkalinity such as ammonia does not impact the analysis of amine.

Conclusion

Near Infrared (NIR) technology has been an attractive metrology of ammonium and amine in PERR due to its real-time, non-contact, and non-reagent monitoring capabilities. Alternative metrologies (titrimetric, electro-chemical, photometric, IC, etc) can be preferable depending on solution complexity and process control requirements.

References

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2. E. Shalyt, G. Liang, P. Bratin, C. Lin, "Real Time Monitoring for Control of Cleaning and Etching Solution" (Proceed. of SPWCC Conference, USA, 2007).
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