

Analysis of Impurities in Semiconductor Grade TMAH Using the Agilent 7500cs Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

Application

Semiconductor

Author

Junichi Takahashi Kouichi Youno Agilent Technologies 9-1 Takakura-Cho, Hachioji-Shi Tokyo, 192-0033 Japan

Abstract

This application note demonstrates the suitability of a newly developed, high sensitivity reaction cell inductively coupled plasma mass spectrometer (ICP-MS) for the determination of inorganic impurities in semiconductor-grade tetramethyl ammonium hydroxide (TMAH). The Agilent 7500cs ICP-MS, which features a high sensitivity version of the Octopole Reaction System (ORS), was used to analyze TMAH for all the metals according to Semiconductor Equipment and Materials International (SEMI) Tier A specifications. The ORS eliminates all plasma and matrix based polyatomics that interfere with the measurement of elements such as K, Mg, Ca, AI, Cr, Fe, Co, Ni, and Cu and provides excellent ion transmission and sensitivity. All analytes can be measured at high plasma power to promote complete decomposition of the TMAH in the plasma. Sample preparation is a simple 5× dilution of the 25% TMAH solution in deionized water, followed by direct analysis by the ICP-MS.

Introduction

TMAH is used in large volumes during the production of semiconductors and thin film transistors for liquid crystal displays. It is used to dissolve UVmodified positive photoresist from the surface of silicon wafers. The quality control of TMAH and other reagents that are used as cleaning and stripping agents is critical because they come into direct contact with the wafer surface. Any impurities present in the reagents can have a direct affect on the yield and performance of the final semiconductor device.

The performance data presented in this application note was obtained from the analysis of TMAH (5% w/w) using the Agilent 7500cs Octopole Reaction System (ORS) inductively coupled plasma mass spectrometer (ICP-MS), operating under normal plasma conditions. Data for the full range of elements specified in Semiconductor Equipment and Materials International (SEMI) Tier A specifications includes background equivalent concentrations (BEC), 3-sigma detection limits (DL), 500 ppt spike recoveries, long term stability performance (1 ppb spike, 2 hours), and calibration curves for a range of elements (including Mg, Co, Ni, and Cu) at the low ppt level.



Interference Removal

Matrix-based polyatomic overlaps present specific analytical problems for conventional quadrupole ICP-MS where ultratrace analysis is required in complex sample matrices. With the introduction of the high-sensitivity 7500cs reaction cell ICP-MS, analysts can attenuate matrix interferences using a controlled environment within the ORS cell, which is pressurized with simple cell gases: hydrogen (reaction mode) and helium (collision mode).

Analysis of TMAH

TMAH is a clear, odorless, water-soluble organic compound that is strongly alkaline (comparable to sodium hydroxide and potassium hydroxide). To stop crystalline deposits from forming inside the plasma torch (which may lead to the torch clogging), 25% TMAH is diluted 5 to 10 times in deionized water prior to analysis. The high carbon content of TMAH leads to the formation of matrixbased polyatomic interferences (shown in Table 1) on important elements such as Mg, Al, Cr, Co, Ni, and Cu, which compromises the trace analysis of these elements by conventional (non-reaction cell) ICP-MS. The 7500cs is able to remove these carbon and nitrogen-based interferences, greatly reducing the BEC for these elements. In addition, plasmabased interferences Ar, ArH, and ArO, which interfere with Ca, K, and Fe respectively, are attenuated within the ORS.

 Table 1.
 Matrix-Based Polyatomic Interferences on Mg, AI, Cr, Co, Ni, and Cu

Mass	Analyte
24	Mg
27	AI
52	Cr
59	Со
60	Ni
63	Cu
	Mass 24 27 52 59 60 63

Methodology

Sample Preparation

Sample preparation consisted of simply diluting the concentrated TMAH (25%) 5-fold with ultrapure deionized water, resulting in a 5% (w/w) solution.

Instrumentation

The instrument used in this application was an Agilent 7500cs ICP-MS equipped with an ORS, ShieldTorch System (STS), MFN-100 nebulizer, platinum interface cones and standard quartz sample introduction kit. The standard sample introduction kit consists of a 2.5 mm injector torch. A wide-bore torch is essential to prevent clogging. Instrument operating conditions are given in Table 2.

Table 2. ICP-MS Operating Conditions

Parameter	ICP-MS Conditions
RF power	1600W
Sampling depth	8 mm
Carrier gas flow	0.7 L/min
Makeup gas flow	0.54 L/min

Method of Quantification

Calibrations were performed using matrix-matched TMAH standards. An aliquot of TMAH was spiked to final concentrations of 0, 200, 600, and 1000 ppt using a multi-element standard. The concentration of the analytes present in TMAH was determined against this external calibration. No internal standards were added to avoid the risk of contamination. The use of matrix matched calibration standards provides simpler operation than calibrating each sample using standard addition, but also minimizes errors resulting from sample transport and nebulization effects, which can occur if non-matched standards are used. Concentrations obtained were corrected to account for the $5\times$ dilution factor.

The effectiveness of the external, matrix-matched calibration was gauged by spiking samples with a multielement standard at a concentration of 500 ppt (ng/L) and calculating recoveries. Figure 1 illustrates representative calibration curves in the matrix matched solution for Ca, Co, Ni, and Cu.





Standard Addition × Tune Count/CPS RSD % Mass Elei IS Units Conc Step Lv 5 💌 --- 💌 ppt • 0.00 200.00 600.00 289.00 4200.00 1.23E+04 P 11.30 P 1.57 59 Co 1 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 14 15 16 17 18 19 20 P 1.30 P 1.57 P 2.908 P 2.03 Count/CPS(Y) unweighted 2.90E-02 count/CPS 1000.00 2.04E+04 2.2E+04---------------.... ---------------1.1E+04 ----------------.... -------01 ... ----1200.00 Conc.(X) ppl Enter Curve Fit: Y=aX+[blank]+bkg • Conc.= 1.438E+001 r = 1.0000 ppt Restore Reject Y = 2.010E+001*X +2.890E+002 +bkg bkg = 0.000E+000 Min Conc: 0.00 Next Prev 0K Cancel Help



Figure 1. Calibration curves for Ca, Co, Ni, and Cu in 5% TMAH.

Results

DL and BEC for a full suite of semiconductor elements in TMAH are summarized in Table 3. As the data in the table demonstrates, all elements return DL and BEC at ppt levels (ng/L), even for the more difficult elements. These results highlight the effectiveness of the ORS cell for removing plasma and matrix-based polyatomic interferences in TMAH. The maximum allowed concentrations in 25% TMAH as specified in the SEMI Tier A guidelines is 5 ppb for Na, K, Au, and Fe, and 10 ppb for all other elements.

The 500 ppt spike recoveries data presented in Table 3 are in the SEMI specified range of 75%–125%. The quantitative recovery also indicates the absence of any nebulization or transport interferences. Note: all recoveries were determined without the use of an internal standard, therefore simplifying sample preparation and eliminating a potential source of contamination.

Table 3. DLs (3 sigma), BECs and Spike Recoveries at 500 ppt Level for all SEMI Elements in 5% TMAH

	Plasma					SEMI* Tier A		
Element (mass)	power (W)	H₂ Gas flow (mL∕min)	He gas flow (mL/min)	DL 3 sigma, n = 10 (ppt)	BEC (ppt)	Spec - max level (ppt)	Spike recovery (%) 500 ppt spike	
Li (7)	1600	-	-	1.7	12	2000	100	
Be (9)	1600	-	-	0.40	0.41	2000	97	
B (10)	1600	5.0	-	56	51	2000	97	
Na (23)	1600	5.0	-	5.7	50	1000	91	
Mg (24)	1600	5.0	-	6.3	14	2000	96	
AI (27)	1600	5.0	-	28	230	2000	99	
K (39)	1600	5.0	-	6.5	69	1000	91	
Ca (40)	1600	5.0	-	4.8	16	2000	95	
Cr (52)	1600	5.0	-	9.8	55	2000	96	
Mn (55)	1600	5.0	-	1.2	5.4	2000	94	
Fe (56)	1600	5.0	-	9.2	130	1000	93	
Co (59)	1600	-	5.0	1.5	3.6	2000	92	
Ni (60)	1600	-	5.0	3.4	4.4	2000	89	
Cu (63)	1600	-	5.0	4.9	28	2000	90	
Zn (64)	1600	-	5.0	120	310	2000	84	
Ga (71)	1600	-	5.0	3.9	7.3	2000	96	
Ge (72)	1600	-	5.0	5.3	8.2	2000	90	
As (75)	1600	-	5.0	4.1	5.5	2000	93	
Sr (88)	1600	-	5.0	2.7	3.0	2000	91	
Zr (90)	1600	-	5.0	1.1	1.1	2000	93	
Mo (95)	1600	-	5.0	1.6	2.9	2000	92	
Ag (107)	1600	-	5.0	0.84	2.8	2000	91	
Cd (111)	1600	-	-	0.42	0.33	2000	89	
Sn (118)	1600	-	-	2.1	9.3	2000	91	
Sb (121)	1600	-	-	0.58	1.3	2000	92	
Ba (138)	1600	-	-	0.74	0.73	2000	91	
Au (197)	1600	-	-	0.63	2.2	2000	90	
TI (205)	1600	-	-	0.17	0.21	2000	91	
Pb (208)	1600	-	-	1.4	16	2000	90	
Bi (209)	1600	-	-	0.13	0.54	2000	92	

*Maximum acceptable levels in diluted TMAH (5% w/w).

A long-term stability study was performed by adding a 1 ppb (μ g/L) standard into the 5% TMAH and analyzing the spiked sample over a 2-hour period. Instrument stability over this period was excellent with %RSD values typically 3%–4%. A stability plot of all analyte elements is shown in Figure 2.



Figure 2. Analysis of 1 ppb multi-element standard spiked into 5% TMAH measured repeatedly over a 2-hour period. Analysis time per sample including 60 s of sample uptake was 288 s (0.33 s integration time per mass, three replicate measurements).

Conclusions

A newly developed high sensitivity reaction cell ICP-MS was used to analyze 25% TMAH following a 5-fold dilution for all elements specified in SEMI Tier A Specifications and Guidelines for TMAH. All analytes were measured in a single analytical run with automatic switching of instrument operating parameters (all data was acquired under normal plasma operating conditions, that is 1600W RF forward power) and with the results being combined into a single report automatically. A typical total analysis time for this application is 5 minutes.

The results highlight the effectiveness of the ORS for removing plasma and matrix-based polyatomic interferences on all the analytes of interest. All potential interferences are attenuated using the ORS with simple gases H_2 or He, and the analysis is fast and robust. The 500 ppt spike recovery data demonstrates the effectiveness of operating at high RF power with negligible plasma ionization suppression from the organic sample matrix. The quantitative recoveries also indicate the absence of any nebulization or transport interferences.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem/icpms.

For more information about semiconductor measurement capabilities, go to www.agilent.com/chem/semicon.

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice. $% \left({{{\boldsymbol{x}}_{i}}} \right)$

© Agilent Technologies, Inc. 2003

Printed in the USA July 21, 2003 5988-9892EN

