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Determination of ultratrace elements in semiconductor grade TMAH developer

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Keywords

Element 2, High resolution ICP-MS, Semiconductor analysis, TMAH

Goal

To demonstrate the suitability of the Thermo Scientific™ Element 2™ High Resolution ICP-MS for trace metals analysis in high purity samples, related to the manufacture of semiconductors.

Summary

High-resolution ICP-MS in both hot and cold plasma operating conditions is used to determine sub-ng/g levels of metals in semiconductor grade 0.3 N TMAH developer. Instrumental sensitivity in the TMAH matrix is identical to that in dilute nitric acid with > 1000 cps per pg/g In. High resolution was used to determine the existence of matrix induced polyatomic interferences. The interferences found were of sufficient severity that high resolution had to be used for the analysis of ten of the fifteen trace metals elements investigated. By means of computer controlled switching between low and high resolution and hot and cold plasma conditions, interference-free analysis was possible during a single analysis. Detection limits in TMAH ranged from 0.1 pg/g for Li to 9 pg/g for Cu.

Introduction

0.3 N TMAH (tetramethyl ammonium hydroxide, $(CH_3)_4NOH$) is used during the lithographic process in semiconductor industry. A direct ICP-MS technique provides a useful quality control for pg/g and sub-pg/g metal concentrations in TMAH but this has proven difficult to realize due to the existence of significant matrix-derived interferences as well as non-spectral interferences.

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While cold plasma has been shown to be effective in reducing argon based interferences, it is even more prone to matrix suppression than hot plasma and other polyatomic interferences, previously not found under hot plasma conditions, may be preferentially formed.

However, the use of cold plasma does provide an additional benefit of a reduced background equivalent concentration (BEC) for elements with low first ionization potentials.

The Thermo Scientific™ Element 2™ HR-ICP-MS has been shown to be resistant to matrix effects in complicated matrices, such as organic solvents, providing sensitivities that can approach those in water. In this application report, the suitability of the Element 2 HR-ICP-MS with its high mass resolution, high sensitivity and hot and cold plasma capabilities will be assessed for the direct analysis of 0.3 N TMAH. Analytically determined concentration data will be reported as well as limits of detection for the fifteen elements measured.

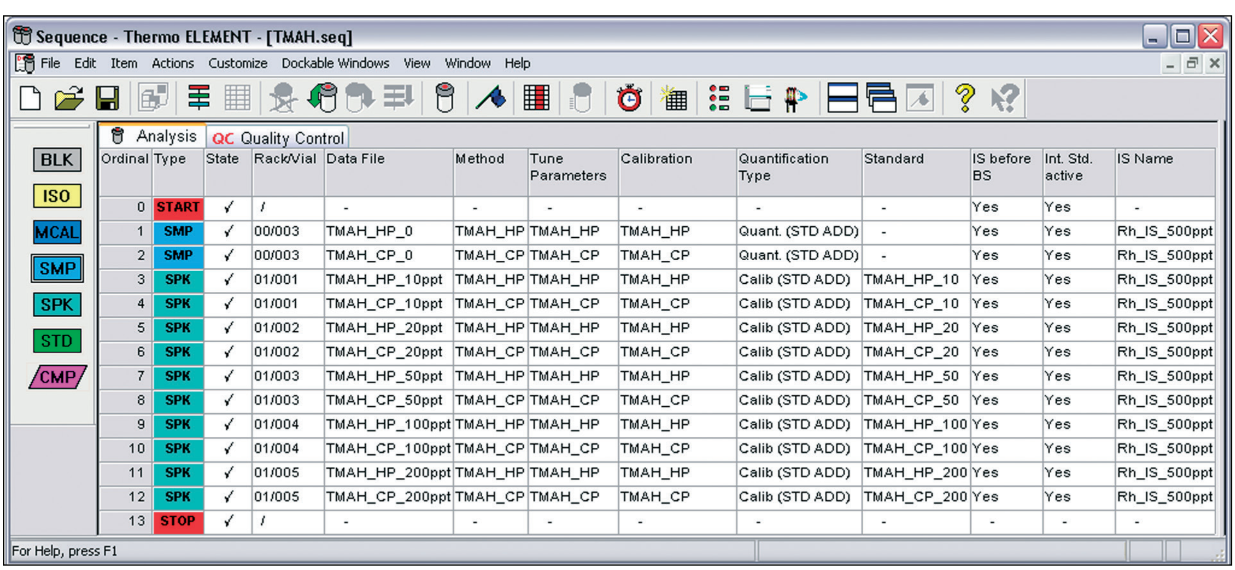
Experimental

The sample introduction equipment used and instrumental operating conditions are shown in Table 1. Sample analysis was carried out completely unattended using an autosampler and software controlled switching between hot and cold plasma conditions and resolution settings. The spreadsheet display from the Thermo Scientific™ Element 2 Software is shown in Figure 1.

Table 1. Sample introduction equipment and instrumental operating conditions used for the analysis of 0.3 N TMAH.

Sample introduction equipment and operating parameters	
100 µL/min self-aspirating PFA concentric nebulizer (Micro-Flow PFA-100, ESI, Omaha, NE, USA)	
PFA spray chamber	
Demountable quartz torch with sapphire injector	
Ni sampling and skimmer cones	
Hot plasma conditions	
Forward power	1030 W
Sample gas flow	0.94 L/min
Focus Lens	- 820 V
Cold plasma conditions	
Forward power	725 W
Sample gas flow	1.00 L/min
Focus Lens	- 1000 V

Note: All other instrument settings are identical for the two plasma conditions.



Ordinal	Type	State	Rack/Vial	Data File	Method	Tune Parameters	Calibration	Quantification Type	Standard	IS before BS	Int. Std. active	IS Name
0	START	✓	/	-	-	-	-	-	-	Yes	Yes	-
1	SMP	✓	00/003	TMAH_HP_0	TMAH_HP	TMAH_HP	TMAH_HP	Quant. (STD ADD)	-	Yes	Yes	Rh_IS_500ppt
2	SMP	✓	00/003	TMAH_CP_0	TMAH_CP	TMAH_CP	TMAH_CP	Quant. (STD ADD)	-	Yes	Yes	Rh_IS_500ppt
3	SPK	✓	01/001	TMAH_HP_10ppt	TMAH_HP	TMAH_HP	TMAH_HP	Calib (STD ADD)	TMAH_HP_10	Yes	Yes	Rh_IS_500ppt
4	SPK	✓	01/001	TMAH_CP_10ppt	TMAH_CP	TMAH_CP	TMAH_CP	Calib (STD ADD)	TMAH_CP_10	Yes	Yes	Rh_IS_500ppt
5	SPK	✓	01/002	TMAH_HP_20ppt	TMAH_HP	TMAH_HP	TMAH_HP	Calib (STD ADD)	TMAH_HP_20	Yes	Yes	Rh_IS_500ppt
6	SPK	✓	01/002	TMAH_CP_20ppt	TMAH_CP	TMAH_CP	TMAH_CP	Calib (STD ADD)	TMAH_CP_20	Yes	Yes	Rh_IS_500ppt
7	SPK	✓	01/003	TMAH_HP_50ppt	TMAH_HP	TMAH_HP	TMAH_HP	Calib (STD ADD)	TMAH_HP_50	Yes	Yes	Rh_IS_500ppt
8	SPK	✓	01/003	TMAH_CP_50ppt	TMAH_CP	TMAH_CP	TMAH_CP	Calib (STD ADD)	TMAH_CP_50	Yes	Yes	Rh_IS_500ppt
9	SPK	✓	01/004	TMAH_HP_100ppt	TMAH_HP	TMAH_HP	TMAH_HP	Calib (STD ADD)	TMAH_HP_100	Yes	Yes	Rh_IS_500ppt
10	SPK	✓	01/004	TMAH_CP_100ppt	TMAH_CP	TMAH_CP	TMAH_CP	Calib (STD ADD)	TMAH_CP_100	Yes	Yes	Rh_IS_500ppt
11	SPK	✓	01/005	TMAH_HP_200ppt	TMAH_HP	TMAH_HP	TMAH_HP	Calib (STD ADD)	TMAH_HP_200	Yes	Yes	Rh_IS_500ppt
12	SPK	✓	01/005	TMAH_CP_200ppt	TMAH_CP	TMAH_CP	TMAH_CP	Calib (STD ADD)	TMAH_CP_200	Yes	Yes	Rh_IS_500ppt
13	STOP	✓	/	-	-	-	-	-	-	-	-	-

Figure 1. Sequence table from the Thermo Scientific Element 2 Software Suite.

Sensitivity in the TMAH Matrix

The Element 2 HR-ICP-MS, with a specified sensitivity of > 1 Mcps per ng/g for ^{115}In in low resolution and detector dark noise of < 0.2 cps, has been shown to be ideally suited for the determination of ultratrace metal impurities in high purity water. The Element 2 HR-ICP-MS has been shown to be resistant to matrix effects, delivering instrumental performance in TMAH comparable to that obtained in water. Instrumental sensitivity in TMAH is identical to that in dilute nitric acid with > 1000 cps per pg/g In. These high sensitivities allow the Element 2 HR-ICP-MS to analyze TMAH at low pg/g levels without any sample preparation, thus ensuring a high sample throughput in a routine laboratory environment.

Identification of Polyatomic Interferences

As part of method development, a TMAH sample was scanned for interferences under both hot and cold plasma conditions. Matrix induced interferences were identified that made the use of medium resolution (R = 4000) necessary for interference-free quantification of ten of the fifteen elements examined (Table 2).

Table 2. Elements analyzed, plasma operating conditions and polyatomic interferences identfied in 0.3 N TMAH.

Isotope	Plasma conditions	Interferences identified
^{24}Mg	Hot	$^{12}C_2$
^{27}Al	Cold	$^{12}C^{15}N$, $^{13}C^{14}N$
^{39}K	Cold	^{38}ArH, $H_2{}^{18}OH_3{}^{16}O$
^{44}Ca	Cold	$^{12}C^{16}O_2$, $^{30}Si^{14}N$, $^{12}C_2H_6{}^{14}N$
^{47}Ti	Hot	$^{15}N^{16}O_2$, $^{14}N^{16}O_2H$
^{52}Cr	Cold	$^{40}Ar^{12}C$
^{55}Mn	Cold	$^{40}Ar^{15}N$, $^{12}CH^{14}N_3$, $(H_2{}^{16}O)_3H$
^{56}Fe	Cold	$^{40}Ar^{16}O$, $^{12}C_2{}^{13}CH_5{}^{14}N$
^{60}Ni	Cold	$^{12}C_2H_6{}^{14}N^{16}O$
^{66}Zn	Hot	$^{40}Ar^{12}C^{14}N$

For example, the direct analysis of manganese at *m/z* 55 under hot plasma conditions is complicated by interferences from $^{40}Ar^{15}N$ and $^{40}Ar^{14}NH$ generated by the sample matrix (Figure 2). Argon based interferences can be reduced or even eliminated by cold plasma parameters. However, the use of cold plasma does not ensure interference-free analysis as, with even relatively simple matrices, new interferences that are not generated with hot plasma conditions can be shown to occur.

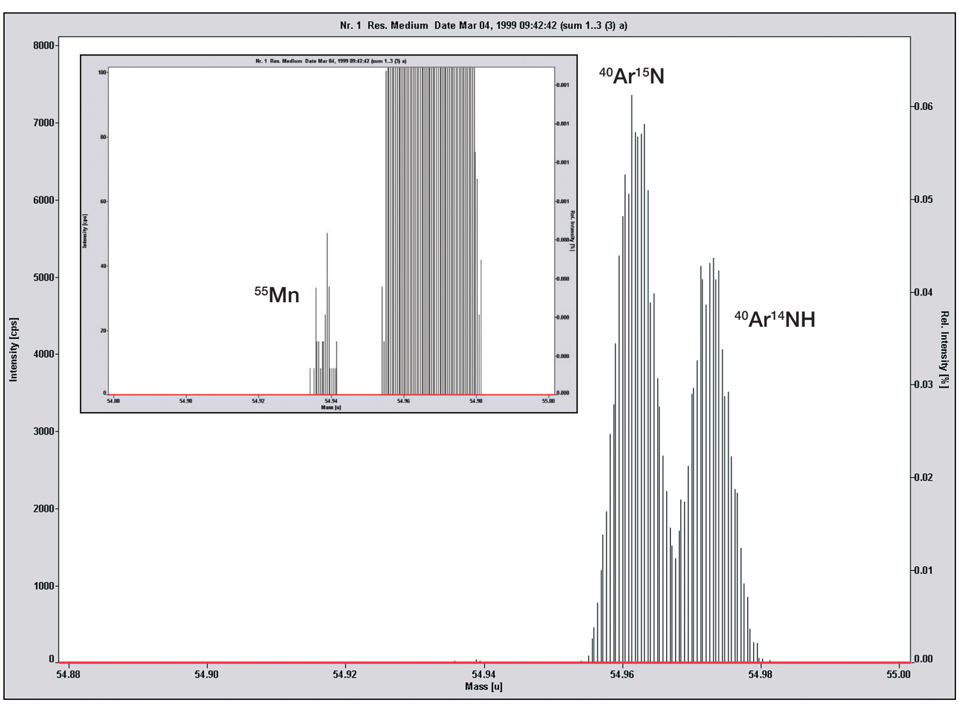


Figure 2. Medium resolution (R = 4000) spectrum of manganese (*m/z* 55) showing $^{40}Ar^{15}N$ and $^{40}Ar^{14}NH$ interferences generated by the TMAH matrix.

For example, Figure 3 shows the polyatomic interferences observed at the nominal mass of 56 amu, the major isotope of iron, under both hot and cold plasma conditions. As expected the $^{40}Ar^{16}O$ interference at *m/z* 56 is greatly reduced with cold plasma, but is not completely removed. A new additional interference, preferentially formed under cold plasma conditions is seen, clearly demonstrating that high resolution is necessary, even with cold plasma, to guarantee interference free analysis.

Results

Fully quantitative analysis of fifteen elements in a 0.3 N TMAH sample was performed using a standard addition calibration in the sample matrix with spike concentrations of 10 to 200 pg/g, depending on the element. An internal standard (500 pg/g Rh) was added to all samples. Figure 4 shows the addition calibration line obtained for Na (low resolution and cold plasma) and Fe (medium resolution and cold plasma) in the TMAH matrix.

Here the benefit of a low BEC using cold plasma operating conditions can be seen, allowing low pg/g concentrations to be determined accurately. Concentration data and detection limits for the fifteen elements determined by direct analysis of 0.3 N TMAH are presented in Table 3. The detection limits were calculated as the analyte concentration equivalent to 3 times the standard deviation from ten replicate on-peak analyses of the 0.3 N TMAH blank.

Table 3. Concentration data for the 0.3 N TMAH sample, as well as detection limits for the fifteen elements determined.

Isotope	Plasma conditions	Resolution	Concentration (pg/g)	Detection limit (pg/g)
^{7}Li	Cold	LR	13.4	0.1
^{11}B	Hot	LR	177	8.7
^{23}Na	Cold	LR	55.2	4.8
^{63}Cu	Cold	LR	13.5	9.2
^{208}Pb	Cold	LR	2.3	0.7
^{24}Mg	Hot	MR	12.8	8.2
^{27}Al	Cold	MR	33.5	1.3
^{39}K	Cold	MR	21.3	0.4
^{44}Ca	Cold	MR	135	0.9
^{47}Ti	Hot	MR	67.1	6.1
^{52}Cr	Cold	MR	11.7	2.2
^{55}Mn	Cold	MR	4.9	1.2
^{56}Fe	Cold	MR	37.4	8.4
^{60}Ni	Cold	MR	7.7	6.9
^{66}Zn	Hot	MR	42.5	4.8

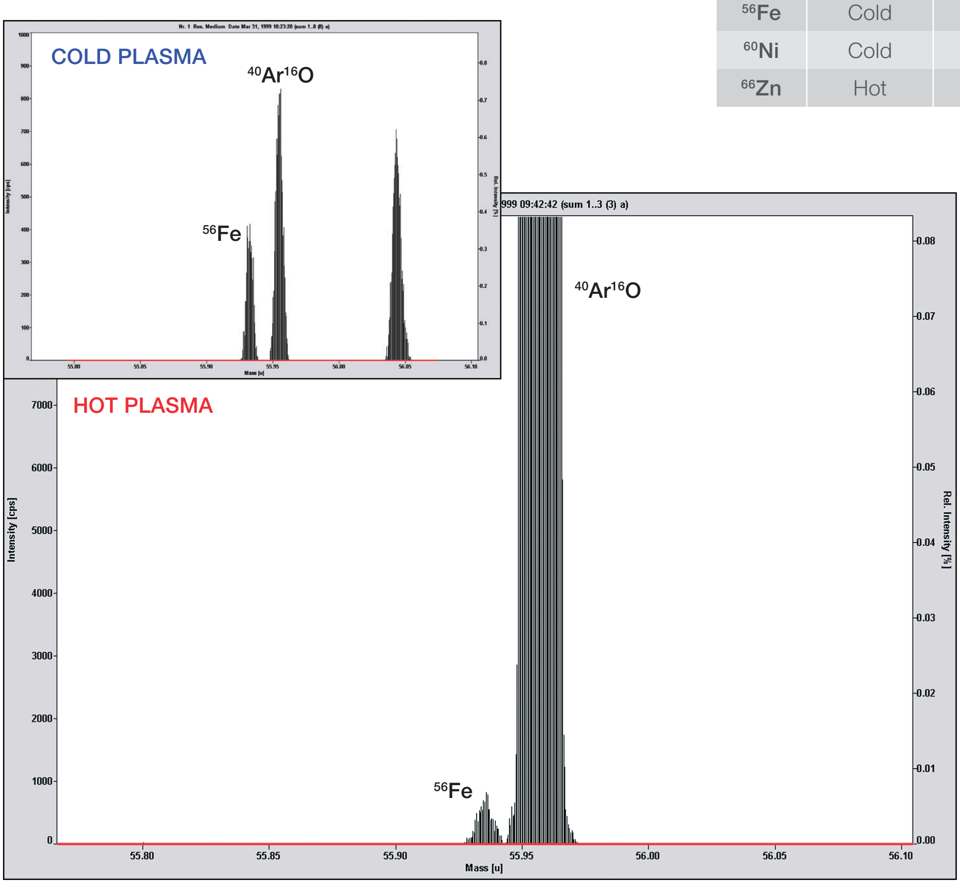


Figure 3. Medium resolution (R = 4000) of iron (*m/z* 56) showing the difference polyatomic interferences observed under hot and cold plasma conditions.

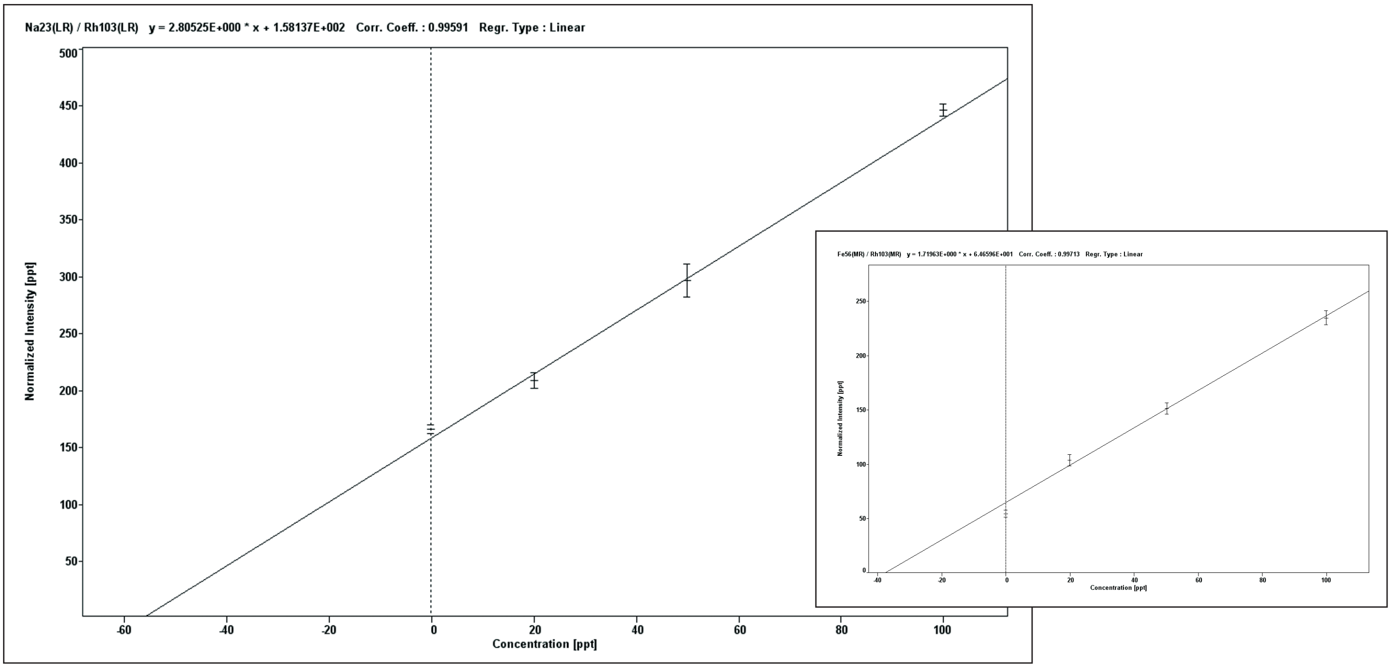
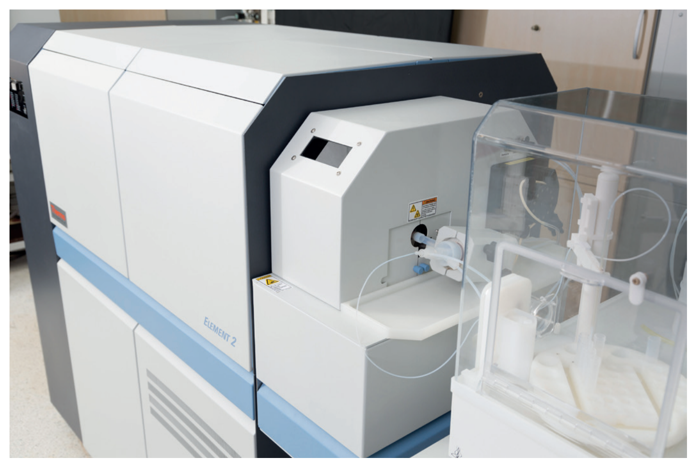


Figure 4. Calibration lines obtained for Na (low resolution, cold plasma) and Fe (medium resolution, cold plasma) in the TMAH matrix.

Conclusions

The Element 2 HR-ICP-MS is shown suitable for the direct, routine quantification of trace elemental concentrations at the pg/g level in 0.3 N TMAH. Sample matrix induced interferences specific to either hot or cold plasma operating conditions, are shown to require the use of medium resolution (R = 4000) for the interference free analysis of ten (Mg, Ti and Zn for hot plasma and Al, K, Ca, Cr, Mn, Fe and Ni with cold plasma) of the fifteen elements determined. The high sensitivity in the sample matrix and low dark noise of the Element 2 HR-ICP-MS enable sub pg/g detection limits.



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