Application Note: 30072

Determination of Ultratrace Elements in Semiconductor Grade TMAH Developer by High Resolution ICP-MS

Key Words

- Finnigan™ ELEMENT 2
- High Resolution ICP-MS
- Semiconductor Analysis
- TMAH

Summary

High-resolution sector-field 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 would provide 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. 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.

Because the Finnigan ELEMENT 2 has been shown to be more resistant to matrix effects than quadrupole ICP-MS[1], sensitivities in complicated matrices, such as organic solvents, can approach those in water. In this application report, the suitability of the Finnigan ELEMENT 2 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 a CETAC ASX-100 autosampler and software controlled switching between hot and cold plasma conditions and resolution settings. The spreadsheet display from the Finnigan ELEMENT 2 Sequence Editor is shown in Figure 1.

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: 0.940 L/min
Focus Lens: - 820 v

COLD PLASMA CONDITIONS
Forward power: 725 W
Sample gas flow: 1.000 L/min
Focus Lens: - 1000 v

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

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

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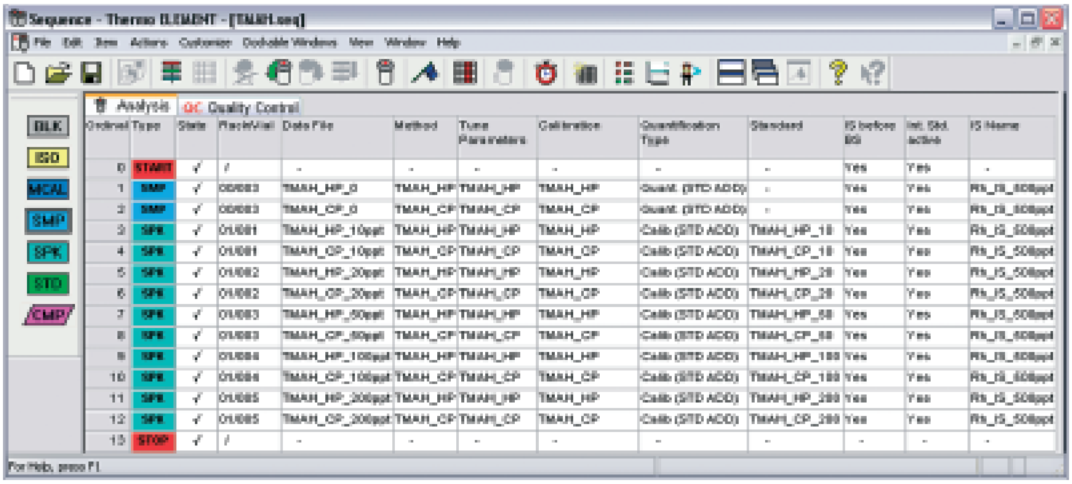

Figure 1: Sequence table from the Finnigan ELEMENT 2 Sequence Editor.

Sensitivity in the TMAH Matrix

The Finnigan ELEMENT 2, with a specified sensitivity of > 1 Mcps per ng/g for ^{115}Indium in low resolution and detector dark noise of < 0.2 cps, has been shown to be ideally suited for the determination of ultra-trace metal impurities in high purity water. Because the Finnigan ELEMENT 2 has been shown to be more resistant to matrix effects than quadrupole ICP-MS[1], instrumental performance in TMAH was expected to be comparable to that obtained in water. The sensitivity under hot plasma operating conditions for 0.3 N TMAH solution spiked with 100 pg/g of a multi-elemental solution containing Li, In and U is shown in Figure 2. Instrumental sensitivity in TMAH is identical to that in dilute nitric acid with > 1000 cps per pg/g In. These high sensitivities allow the Finnigan ELEMENT 2 to analyze TMAH at low pg/g levels without any sample preparation, thus ensuring a high sample throughput in a routine laboratory environment.

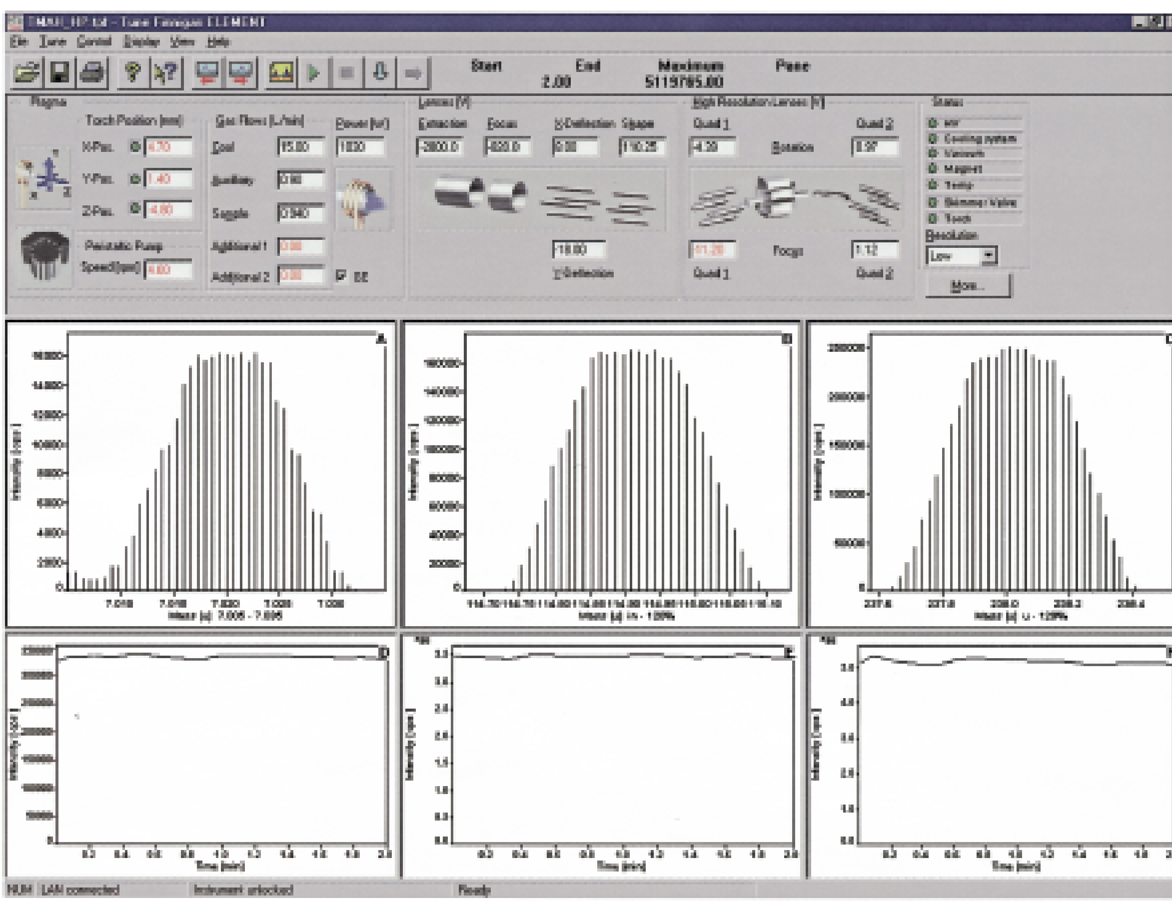

Figure 2: Instrumental sensitivity under hot plasma operating conditions for 0.3 N TMAH solution spiked with 100 pg/g of a multi-elemental solution containing Li, In and U.

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).

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	$^{40}Ar^{12}C^{14}N$

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

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 3). Argon based interferences can be reduced or even eliminated by cold plasma parameters[2]. 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. For example, Figure 4 shows the polyatomic interferences observed at the nominal mass of 56 a.m.u., 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.

Isotope Conditions	Plasma	Resolution (pg/g)	Concentration Limit (pg/g)	Detection
^{7}Li	Cold	LR	13.4	0.12
^{11}B	Hot	LR	177	8.68
^{23}Na	Cold	LR	55.2	4.75
^{63}Cu	Cold	LR	13.5	9.16
^{208}Pb	Cold	LR	2.29	0.74
^{24}Mg	Hot	MR	12.8	8.16
^{27}Al	Cold	MR	33.5	1.31
^{39}K	Cold	MR	21.3	0.44
^{44}Ca	Cold	MR	135	0.87
^{47}Ti	Hot	MR	67.0	6.07
^{52}Cr	Cold	MR	11.7	2.16
^{55}Mn	Cold	MR	4.94	1.16
^{56}Fe	Cold	MR	37.4	8.39
^{60}Ni	Cold	MR	7.71	6.89
^{66}Zn	Hot	MR	42.5	4.78

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

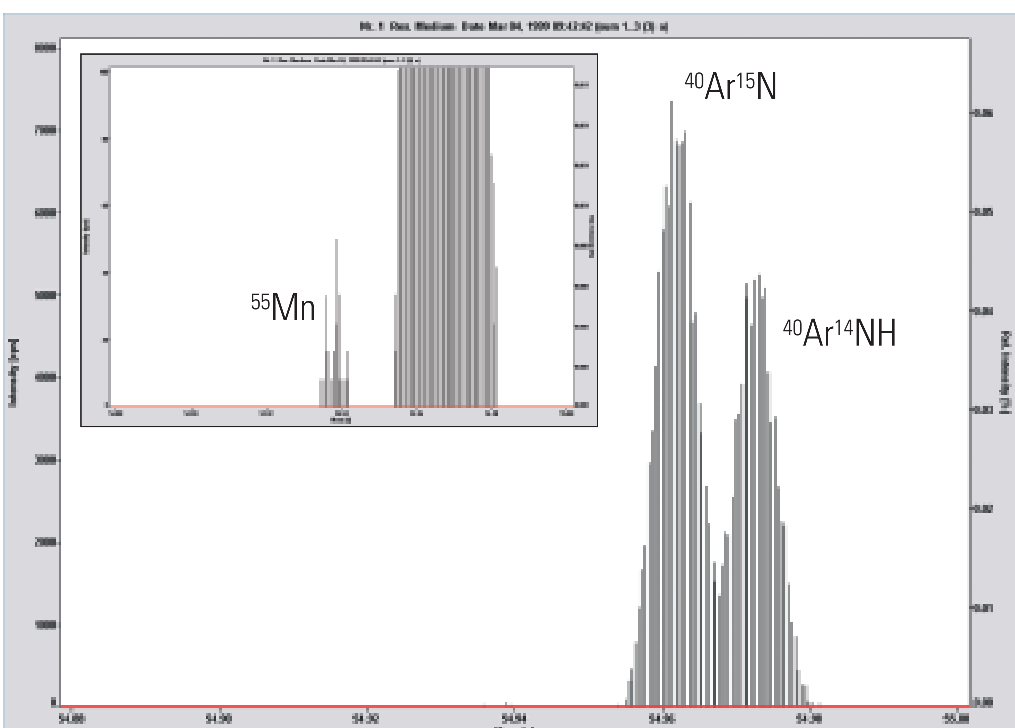

Figure 3: Medium resolution (R = 4000) spectrum of manganese (m/z 55) showing $^{40}Ar^{15}N$ and $^{40}Ar^{14}NH$ interferences generated by the TMAH matrix.

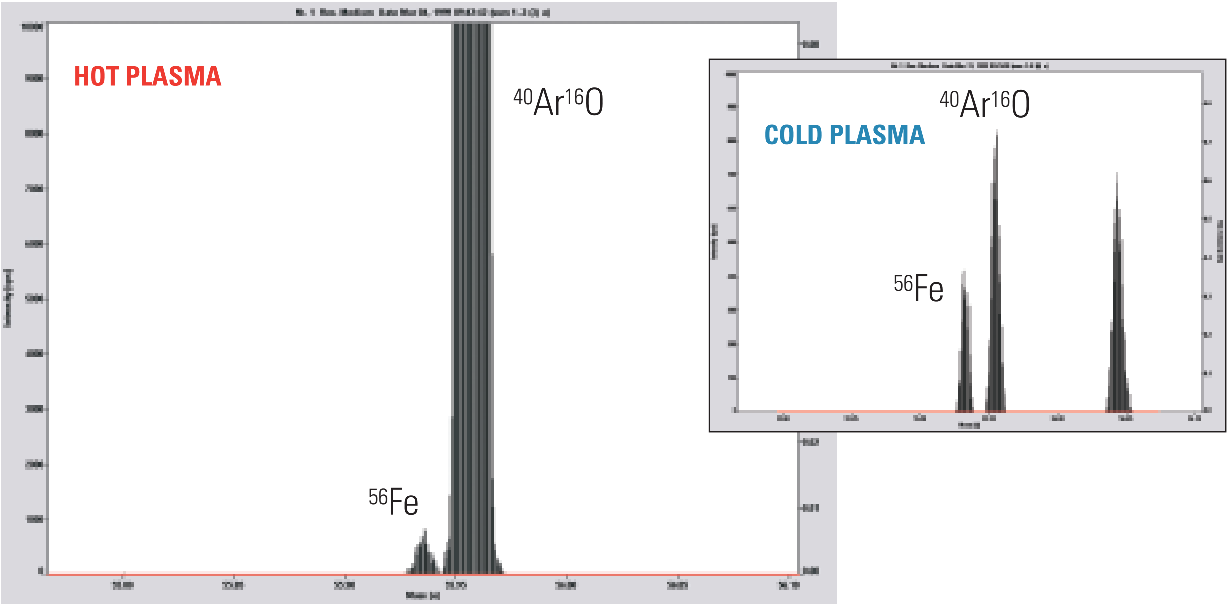

Figure 4: Medium resolution (R = 4000) of iron (m/z 56) showing the difference polyatomic interferences observed under hot and cold plasma conditions.

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 5 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.

Conclusions

The Finnigan ELEMENT 2 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 preclude accurate low concentration level analysis with quadrupole ICP-MS. The use of medium resolution (R = 4000) is therefore necessary 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 Finnigan ELEMENT 2 enable sub pg/g detection limits.

References

[1] Non-spectral interferences caused by a saline water matrix in quadrupole and high resolution ICP-MS. Rodushkin I. and Klockare, D., JAAS, 1998, 13, 159-166

[2] Order of magnitude improvement in sector-field ICP-MS performance using a Pt guard electrode. Wiederin D. and Hamester M. 1998 Winter Conference on Plasma Spectrochemistry, Scottsdale, AZ, 5-10/1/1998, USA

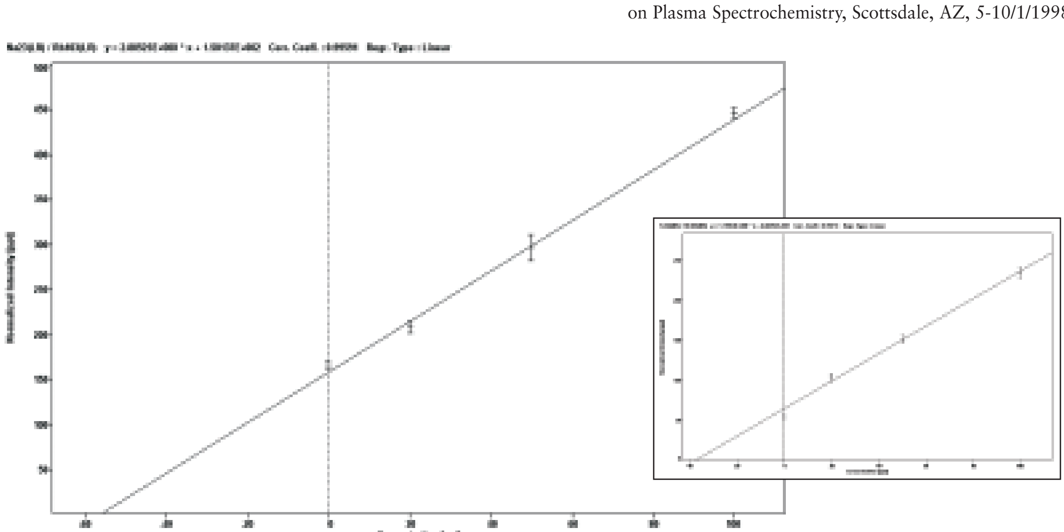

Figure 5: Calibration lines obtained for Na (low resolution, cold plasma) and Fe (medium resolution, cold plasma) in the TMAH matrix.

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Australia
+61 2 8844 9500
Austria
+43 1 333 50340
Belgium
+32 2 482 30 30
Canada
+1 800 532 4752
China
+86 10 5850 3588
France
+33 1 60 92 48 00
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