Determination of trace elements in ultrapure semiconductor grade sulfuric acid using the Agilent 8900 ICP-QQQ in MS/MS mode

Application note

Semiconductor

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Introduction

In the semiconductor industry, it is extremely important to reduce contamination within the manufacturing process, as particle-, metallic-, or organic-based contaminants degrade the quality and reliability of the final device. Organic materials, such as photoresist polymer patterns, must be thoroughly removed from the surface of the silicon wafer following ion implantation; this cleaning step is performed using a piranha solution; a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). Ensuring a low level of metal impurities in these chemicals is vital to ensure that contamination of the wafer surface is avoided at this stage in the manufacturing process.

Since its inception, ICP-MS has been widely utilized for the analysis of elemental impurities in chemicals and materials used by semiconductor-related industries. More recently, collision/reaction cell (CRC) technology, which was first developed for quadrupole ICP-MS (ICP-QMS), has been implemented to remove polyatomic ions that cause problematic spectral interferences on many analytes. In certain sample matrices, however, not all polyatomic species can be completely removed using CRC-ICP-QMS, hindering accurate measurement of a few important elements at low-levels. For example, high concentration sulfur matrices generate polyatomic ions with a low ionization potential, such as SO^+, which interferes with Ti. Since SO^+ has a high dissociation energy of 5.4 eV, it is not easily dissociated using a CRC operating in collision mode with an inert cell gas.

The Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) has a unique tandem MS configuration, comprising two quadrupole mass filters (Q1 and Q2), separated by an octopole reaction system (ORS^4) cell. The MS/MS configuration allows reaction chemistry to be applied to the most complex and challenging interference problems that hinder ICP-QMS. As more reactive gases (e.g. NH_3 or O_2) can be used in ICP-QQQ in a controlled way, the reaction pathways and product ions formed in the cell are not affected by changes in the sample matrix or by other co-existing analyte ions. Using MS/MS, Ti can be analyzed in a sulfur matrix, using NH_3 reaction gas mode, by measuring a suitable ammonia cluster product ion that is free from polyatomic ion interference. In addition, the new axial acceleration technology of the 8900 ICP-QQQ, which accelerates product ions generated in the ORS^4 cell, leads to an increase in sensitivity of product ions, including Ti/NH_3 cluster ions.

In this study, the Agilent 8900 ICP-QQQ was used for the analysis of 42 analytes in sulfuric acid, including Ti and other elements which are difficult to determine at trace levels in a high sulfur matrix.

Experimental

Sample preparation

All sulfuric acid samples were prepared using pre-cleaned PFA containers. High purity 98% H_2SO_4 (TAMA Chemicals Co. Ltd. Japan) was diluted ten-fold with ultrapure water (UPW). All calibration and quantification was done using the method of standard additions (MSA). Standard solutions were prepared from a mixture of XSTC-331, XSTC-7, XSTC-8 (SPEX CertiPrep, USA) and a Si single element standard (Kanto Chemical Co., Inc., Japan).

Instrumentation

An Agilent 8900 ICP-QQQ (#200, Semiconductor configuration) was used throughout. The sample introduction system comprised a quartz torch with a 2.5 mm i.d. injector, quartz spray chamber, a PFA concentric nebulizer and platinum-tipped interface cones. The sample was self-aspirated using an Agilent I-AS autosampler. MS/MS mode, in which Q1 and Q2 both act as unit mass filters, was used for all measurements. To run ten-fold diluted sulfuric acid routinely, it is recommended that the large (18 mm) insert Pt cone is fitted. Long-term corrosion of internal ICP-MS components can be minimized by fitting the dry pump option and ball-type interface valve kit.

Evaluation of different reaction gases

For multi-element trace analysis, O_2, NH_3, H_2 and He were evaluated as cell gases. O_2 is often used in mass-shift methods to move the target analyte from its elemental ion mass to its oxide product ion mass (MO^+) by setting Q2 to 16 amu higher than Q1 [1]. NH_3 is highly reactive and used as a cell gas in both on-mass mode and mass-shift mode depending on the interference to be removed. H_2 and He were used with O_2 or NH_3, to assist the cell gas reaction process. He cell gas was used in collision mode to eliminate many common background polyatomic interferences.

Results and discussion

As is typical with analyses at the ultra-trace level, the optimum plasma mode (normal or cool plasma) and cell gas type was selected for each element. Most higher-mass analytes are free from significant interference in high-purity reagents, but element-specific optimization is particularly important for the ultra-trace analysis of Ti, V, Cr, Zn, Ge and As, which suffer from S-based polyatomic interferences in a sulfur-matrix. Instrument operating parameters used are shown in Table 1.

Table 1. ICP-QQQ operating parameters.

	Cool-NH_3	NH_3-1 (for Ti and V)	NH_3-2 (for Zn)	O_2	O_2+ H_2 (for P)	He mode[1]
RF power, W	600	1600				
Sampling depth, mm	18.0	8.0				
Carrier gas, L/min	0.7					
Makeup gas, L/min	0.75	0.49				
Extraction lens 1, V	-150	5.3	5.1	5.0		4.5
Extraction lens 2, V	-15	-200		-250	-190	-155
Octopole bias, V	-10.0	-17.0	-13.5	-11.0	-4.0	-100.0
Axial acceleration, V	1.0		0.2	1.0		0.0
Energy discrimination, V	-5.0	-18.2	-20.0	-13.0	-8.0	5.0
NH_3 flow[1], mL/min	2	1	4.5	-	-	-
O_2 flow, mL/min	-	-	-	0.7	0.2	-
He flow, mL/min	1	9	1	-	-	9
H_2 flow, mL/min	-	-	-	-	1	-

[1] High engergy He mode conditions

[2] 10% NH_3 balanced with 90% He

O_2 mass-shift mode for As, Se and Si

Oxygen mass-shift mode detects analyte ions (M^+) as reaction product ions at the oxide ion mass (MO^+). For example, $^{75}As^+$ is detected as AsO^+ at *m/z* 91. This method is used when the analyte ion reacts efficiently with O_2 gas to form an oxide ion, while the interfering ion reacts slowly or not at all with the O_2 gas, so does not contribute significantly to the signal at the new mass of the analyte product ion. The lowest detection limits (DLs) and background equivalent concentrations (BECs) for Si, As and Se were obtained with a relatively high O_2 cell gas flow rate (0.7 mL/min), which encourages the formation of O-atom addition product ions for these analytes, especially Se.

O_2 + H_2 mass-shift mode for P

In a sulfur matrix, on-mass measurement of ^{31}P is affected by the peak tail of the large adjacent ^{32}S peak. This can be addressed using ICP-QQQ, which benefits from the high abundance sensitivity (AS) of MS/MS mode. The AS in MS/MS mode is the product of the AS of the two quadrupoles, so Q1 AS x Q2 AS. On the Agilent 8900, each of the two quadrupoles has an AS specification of 10^{-7}, so the overall AS is theoretically 10^{-14}, meaning that peak tailing, even from very intense background peaks, is practically eliminated. However, on-mass measurement (e.g. using He mode) does not give sufficiently low backgrounds for the measurement of P at ultra-trace levels. As an alternative, O_2 mass-shift mode can be used to effectively eliminate the NO^+ or NOH^+ interference on P^+, since the oxidation of P^+ is exothermic, while the oxidation of NO^+ or NOH^+ is endothermic. Hence, these background polyatomic ions are avoided by shifting the P^+ away from the interfering ions, and measuring it as the PO^+ product ion at *m/z* 47. Interestingly, P sensitivity was improved 1.5 times by adding H_2 gas to the cell together with O_2. In this study, O_2 + H_2 mass-shift mode was used for P analysis to obtain maximum sensitivity. However, O_2 alone would deliver sufficient performance for the analysis of semiconductor grade H_2SO_4. Optimum gas conditions were 0.2 mL/min of O_2 and 1 mL/min of H_2.

NH_3 mass-shift mode for Ti

The two most abundant isotopes of titanium, ^{48}Ti and ^{46}Ti, suffer interferences from $^{32}S^{16}O$ and $^{32}S^{14}N$ respectively, so the minor isotope, ^{47}Ti, is usually selected for analysis using ICP-QMS. However, MS/MS mode with ICP-QQQ allows control of the complex reaction chemistry that occurs with ammonia cell gas, allowing the major Ti isotopes to be measured as a suitable Ti-NH_3 cluster ion and thereby avoiding the S-based interferences. Single ng/L level BECs can be achieved using this approach [2]. ^{48}Ti could also potentially suffer an isobaric overlap from the minor ^{48}Ca isotope (0.187% abundance), but this is not a problem in semiconductor reagents as the concentration of Ca is low.

When a heavy cell gas such as O_2 or NH_3 is used at a high flow rate, analyte ions entering the cell significantly slow down due to suffering multiple collisions with the cell gas molecules, resulting in an increased transit time through the cell. Some ions may even lose so much energy that their progress through the cell stops, which causes a loss of sensitivity. Furthermore, product ions formed in the cell are generally very slow as a result of the reaction with cell gas molecules. If the transmission of these product ions through the cell reduces, so does the sensitivity. The ORS^4 CRC of the 8900 Semiconductor configuration ICP-QQQ benefits from axial acceleration; an electrical field is established by a potential gradient in the axial direction of the cell so that positively charged analyte ions are accelerated towards the cell exit. Axial acceleration can improve the transmission of slow-moving product ions, and thus increase the sensitivity for certain analytes. In practice, changing the axial acceleration voltage from 0 V to +1 V resulted in a 5-fold increase in the sensitivity of the ammonium cluster ion selected for titanium analysis, $^{48}TiNH(NH_3)_3^+$ ($m/z = 114$). An axial acceleration voltage of 1 V was used for Ti analysis using MS/MS mass-shift mode with NH_3 cell gas.

Multi-element analysis

Representative calibration curves obtained using MSA are shown in Figure 1. Good linearity was observed for all analytes (R > 0.9995), and sub-ppt detection limits were achieved for all elements apart from Si (44 ppt), P (3 ppt), and Zn (1.5 ppt). The quantitative results of the analysis of 9.8% H_2SO_4 are shown in Table 2. The DLs were determined from 10 x replicate measurements of the blank 9.8% H_2SO_4 solution. Recoveries and RSDs were determined from 10 replicate measurements of a 20 ng/L spiked solution of 9.8 % H_2SO_4. Excellent performance was achieved for all elements, including Ti, V and Zn, indicating the effective suppression of S-based matrix interferences.

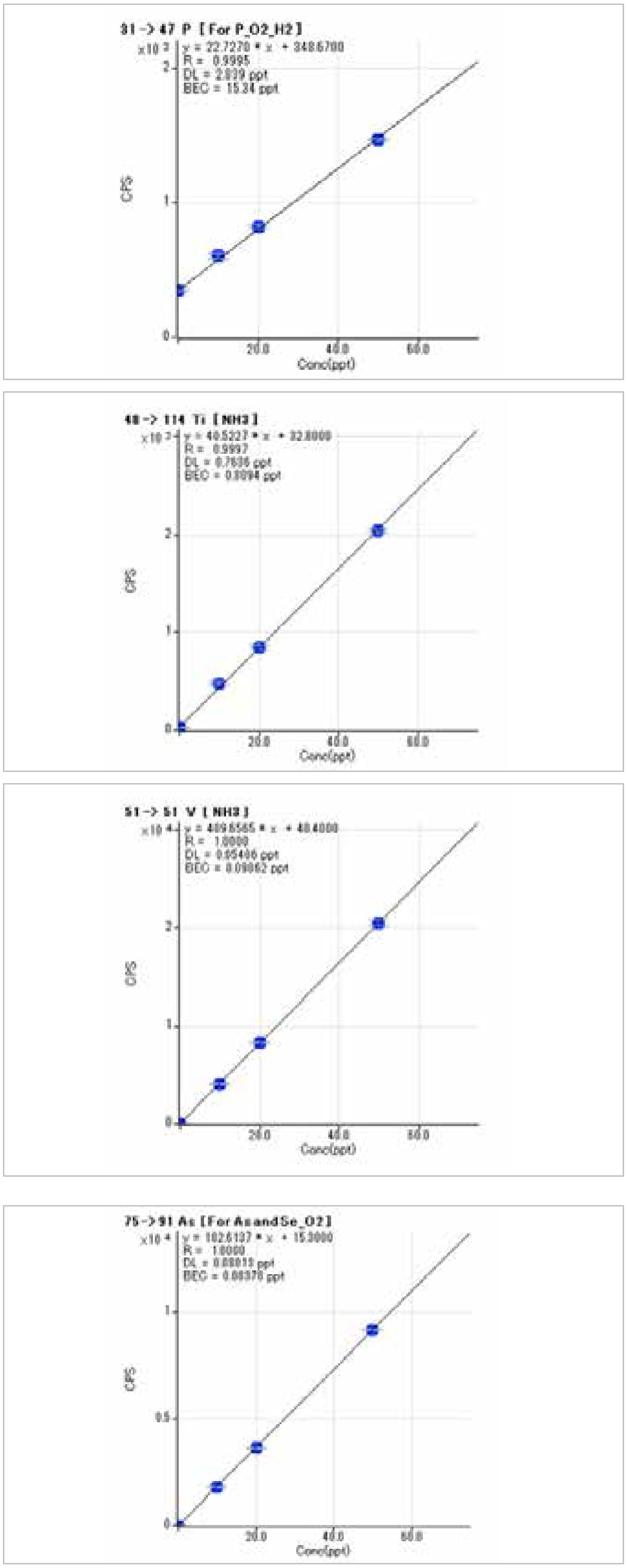

Figure 1. Calibration curves of P, Ti, V and As in 9.8% H_2SO_4

Table 2. Quantitative results for 42 elements in 9.8% H_2SO_4.

Analyte	Mode	Q1 Mass	Q2 Mass	DL (ng/L)	BEC (ng/L)	20 ng/L Spike Recovery (%)	20 ng/L RSD (%)
Li	Cool-NH_3	7	7	0.13	0.13	104	2.1
Na	Cool-NH_3	23	23	0.37	0.73	102	1.8
Mg	Cool-NH_3	24	24	0.15	0.05	106	2.4
Al	Cool-NH_3	27	27	0.18	0.09	107	1.8
Si	O_2	28	44	44	480	*98	*1.7
P	$O_2 + H_2$	31	47	2.8	15	96	3.5
K	Cool-NH_3	39	39	0.36	0.66	104	2.1
Ca	Cool-NH_3	40	40	0.57	0.18	106	1.8
Ti	NH_3-1	48	114	0.76	0.81	99	2.9
V	NH_3-1	51	51	0.05	0.10	101	0.5
Cr	Cool-NH_3	52	52	0.51	0.37	106	2.8
Mn	Cool-NH_3	55	55	0.16	0.11	103	3.0
Fe	Cool-NH_3	56	56	0.40	0.28	101	2.7
Ni	Cool-NH_3	58	58	0.12	0.02	100	3.6
Co	Cool-NH_3	59	59	0.23	0.03	102	2.3
Cu	Cool-NH_3	63	63	0.57	0.58	101	2.8
Zn	NH_3-2	68	85	1.5	1.8	99	4.1
Ga	Cool-NH_3	69	69	0.08	0.01	102	2.0
Ge	He	74	74	0.40	0.24	101	3.3
As	O_2	75	91	0.08	0.08	101	1.1
Se	O_2	78	94	0.14	0.22	103	2.0
Rb	Cool-NH_3	85	85	0.12	0.03	102	2.6
Sr	He	88	88	0.02	0.004	100	1.9
Zr	He	90	90	0.03	0.005	101	1.1
Nb	He	93	93	0.03	0.05	100	1.3
Mo	He	98	98	0.19	0.12	104	1.9
Ru	He	101	101	0.19	0.10	101	3.6
Pd	He	105	105	0.04	0.004	102	3.1
Ag	He	107	107	0.16	0.15	99	1.2
Cd	He	114	114	0.16	0.04	102	3.5
In	He	115	115	0.02	0.008	101	1.1
Sn	He	118	118	0.35	0.33	102	2.3
Sb	He	121	121	0.09	0.03	101	3.1
Cs	He	133	133	0.10	0.17	103	1.7
Ba	He	138	138	0.03	0.007	102	1.3
Ta	He	181	181	0.26	0.42	100	1.6
W	He	182	182	0.28	0.07	99	4.4
Au	He	197	197	0.41	0.30	99	3.3
Tl	He	205	205	0.09	0.07	100	2.6
Pb	He	208	208	0.56	0.93	95	4.1
Bi	He	209	209	0.03	0.004	100	2.2
U	He	238	238	0.02	0.003	101	2.7

*2 µg/L spike

Conclusions

Forty-two elements were determined successfully at ultra-trace levels in semiconductor grade H_2SO_4 using the Agilent 8900 Semiconductor configuration ICP-QQQ. Excellent spike recoveries for all elements were achieved at the 20 ppt level (2 ppb for Si) in the 1/10 diluted H_2SO_4, demonstrating the suitability of the 8900 ICP-QQQ method for the routine analysis of high purity process chemicals.

Problematic spectral interferences that hinder the measurement of some key elements by ICP-QMS were eliminated using ICP-QQQ in MS/MS mode with suitable reaction cell gas conditions. The axial acceleration function of the 8900 ICP-QQQ provided significant improvements in the product ion sensitivity used for the determination of Ti, Zn and P etc. Sub-ppt level DLs and BECs were obtained for almost all analytes in 9.8 % H_2SO_4.

References

1. 'Agilent 8800 Triple Quadrupole ICP-MS: Understanding oxygen reaction mode in ICP-MS/MS', Agilent publication, 2012, 5991-1708EN.

2. J. Takahashi, 'Determination of challenging elements in ultrapure semiconductor grade sulfuric acid by Triple Quadrupole ICP-MS', Agilent publication, 2015, 5991-2819EN

More information

When analyzing 9.8% sulfuric acid on a routine basis, it is recommended to use the following options:

- G3280-67056 Pt sampling cone (18 mm insert)
- G4915A Upgrade to dry pump
- G3666-67030 Interface valve kit - ball type valve

www.agilent.com/chem

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