

Improvement of ICP-MS detectability of phosphorus and titanium in high purity silicon samples using the Agilent 8800 Triple Quadrupole ICP-MS

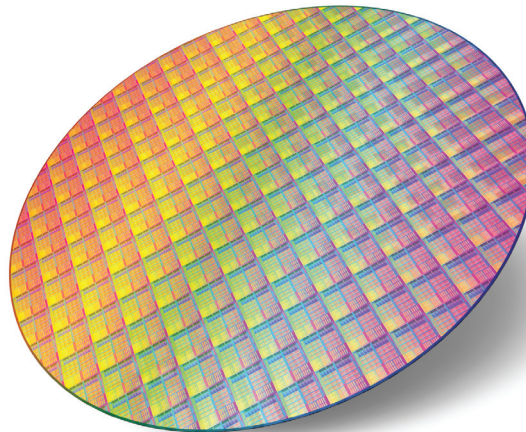
Application note

Semiconductor

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Introduction

In the past three decades monitoring and controlling metallic impurities in semiconductor device manufacturing has become increasingly important. During the period between 1983 and 1985, the first generation of commercial ICP-MS appeared on the market. These first generation ICP-MS systems had high enough sensitivity to determine many trace elements, such as Rare Earth Elements, uranium and thorium, which were free from interference, but could not determine important elements such as potassium, calcium, chromium and iron at low levels because of high background signals from interfering polyatomic ions.

In 1994 HP (Agilent) introduced the 4500 ICP-MS, which included the first reliable commercial implementation of cool plasma operation, and the analysis of trace alkaline and transition metals became possible. In fact, argon and argon-based polyatomic ions could be completely eliminated by



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cool plasma technology, enabling ICP-MS to measure the complete suite of metals typically monitored in high-purity semiconductor chemicals. Due to the success of ICP-MS using cool plasma, it became a vital instrument in the field of semiconductor manufacturing. The main downside of cool plasma was its poor tolerance of high matrix samples, as the lower-power plasma suffered a greater degree of ionization suppression compared to normal “hot” plasma conditions. Cool plasma is not ideal for the routine analysis of high-matrix samples, as the less efficient decomposition of the matrix also leads to more deposition of material on the interface cones and ion lens. The development of collision/reaction cell (CRC) technology in quadrupole ICP-MS (ICP-QMS) offered an alternative means to remove the intense polyatomic backgrounds. Hydrogen or ammonia reaction gas is introduced into the cell to neutralize the argon and argon-based polyatomic ions, as a result of which, trace Ca and Fe can be determined even under a hot plasma conditions. Moreover, helium collision mode can be utilized to reduce or remove other (matrix-based) polyatomic ions, eliminating sulfur- and chlorine-based interferences on other key semiconductor analytes.

However, even the performance of collision/reaction cell is not sufficient for some of the most intense and problematic interferences on the analytes considered “difficult” by ICP-QMS. Analysis of phosphorus and titanium in silicon-rich samples is an example where improved performance is required. Phosphorus is monoisotopic at m/z 31 and a high silicon matrix will lead to a polyatomic ion $^{30}\text{SiH}^+$ which interferes with $^{31}\text{P}^+$. Surface layer contamination of silicon wafers is measured using an etch with HF vapor known as VPD (vapor phase decomposition), and samples prepared in this way usually contain both Si and HF. In this matrix, Si will form the polyatomic ions SiF^+ as well as SiO^+ , making trace analysis of Ti in VPD samples nearly impossible because of the interferences from:

- . $^{30}\text{Si}^{16}\text{O}^+$ on $^{46}\text{Ti}^+$
- . $^{28}\text{Si}^{19}\text{F}^+$ on $^{47}\text{Ti}^+$
- . $^{29}\text{Si}^{19}\text{F}^+$ and $^{30}\text{Si}^{18}\text{O}^+$ on $^{48}\text{Ti}^+$
- . $^{30}\text{Si}^{19}\text{F}^+$ on $^{49}\text{Ti}^+$

ICP-QMS with reaction gas mode does not offer a reliable solution to these interferences, because all ions from the sample enter the reaction cell, and so multiple polyatomic ions are created from all the matrix components and other (variable) analytes present in the sample. If any component of the sample changes, the product ions created in the cell will also change, so new and unpredictable overlaps are created.

The development of triple quadrupole ICP-MS technology finally solves these problems, as MS/MS mode controls the reaction processes in the cell, allowing reaction cell gases to be used reliably and routinely. Phosphorus reacts with hydrogen to produce $^{31}\text{PH}_4^+$ which is detected at m/z 35 by the second quadrupole mass analyzer (Q2). Any previously existing ions present as m/z 35 will already have been excluded by the first quadrupole (Q1), which is set to allow transmission of only ions at m/z 31. An alternative method for measuring P in high Si matrix utilizes oxygen reaction gas. Q1 is set to m/z 31 to allow $^{31}\text{P}^+$ into the cell. $^{31}\text{P}^{16}\text{O}^+$ product ion is produced in the cell by reaction with the O_2 cell gas, and is detected by Q2 which is set to m/z 47. $^{30}\text{SiH}^+$ which also occurs at m/z 31 will also pass through Q1 and enter the cell, but SiH^+ does not react with oxygen in the cell and thus will not produce a SiOH^+ product ion that interferes with $^{31}\text{P}^{16}\text{O}^+$. Oxygen cell gas can also be used for titanium determination using the same reaction principle. Q1 will transmit $^{48}\text{Ti}^+$ and any isobaric interfering ions at m/z 48 such as SiF^+ . Only the titanium ions react with oxygen to produce TiO^+ , which can be detected free from overlap by Q2 which is set m/z 64. In this report, such methodology and figures of analytical merit of the Agilent 8800 Triple Quadrupole ICP-MS with MS/MS capability are described with regard to metallic impurity analysis of Si rich samples.

Experimental

Sample preparation

In a VPD scanner, a solution droplet is scanned across the wafer surface to collect the surface contaminants dissolved from the Si matrix by the HF vapor. The scan droplet is usually composed of HF and H₂O₂, and contains a matrix of dissolved Si, the concentration of which is dependent upon the nature of the oxide layer on the Si wafer. The thickness of the silicon oxide layer on a naturally oxidized wafer is less than 1 nm and the resultant scan solution contains 20 to 30 ppm Si at the most. In contrast, a thermally oxidized silicon wafer has a much thicker silicon oxide layer, and the Si concentration in the VPD scan droplet may reach levels up to 2000 ppm in the final solution. We prepared solutions by dissolving bulk silicon to simulate those two types of VPD samples. Approximately 3 g of silicon pieces were cut from a silicon wafer and thoroughly cleaned with 1:1 HCl/HNO₃. After rinsing with ultra-pure water (UPW), pieces were cleaned with HF and re-rinsed with UPW. This process was repeated twice. The silicon pieces were then dissolved with 40 mL each of 38% HF and 68% HNO₃ in a lightly capped PFA bottle. UPW was added to make 3% Si stock solution from which 30 ppm Si and 2000 ppm Si final matrix solutions

were prepared by further diluting with UPW. Therefore, beside silicon and its impurities, the sample solutions contain a high concentration of nitric and hydrofluoric acids.

Instrumentation

Instrument, peripherals and major operating parameters are described below. Because the sample volume of a VPD scan droplet is usually limited to as low as 0.5 mL, an ultralow uptake nebulizer was used. The number of tune modes was also minimized to reduce the total analytical time.

- ICP-MS: Agilent 8800 Triple Quadrupole ICP-MS
- Nebulizer: C-flow 50 PFA nebulizer (uptake volume: 45 µL/min)
- Inert sample introduction system: PFA spray chamber, end cap and connector tube; demountable torch with 2.5 mm internal diameter (i.d.) sapphire injector
- Interface: Pt sampling cone and Pt/Ni skimmer cone
- Reaction cell gases: Oxygen and hydrogen
- Standard solution: Pre-mixed standard solution from SPEX Corporation
- Phosphorus and sulfur standards were prepared from semiconductor grade phosphoric acid and sulfuric acid, respectively

Table 1. Agilent 8800 ICP-QQQ tuning conditions

		Low Si Conc Tuning			High Si Conc Tuning			
	Tune step	Cool	No gas	O ₂	No gas	H ₂	O ₂	
	Stabilization time	sec	5	30	15	5	15	15
	Scan mode		MS/MS			MS/MS		
Plasma								
	RF power	W	600	1600		1600		
	Sample depth	mm	18	8		8		
	Carrier gas	L/min	0.7	0.7		0.7		
	Makeup gas	L/min	0.95	0.56		0.58		
Lenses								
	Extract 1	V	-180	5		0		
	Extract 2	V	-14	-250		-250	-235	-205
Cell								
	He flow	mL/min	-	-	3	-	-	3
	H ₂ flow	mL/min	0.5	-	-	-	10	-
	O ₂ flow	mL/min	-	-	0.5	-	-	0.5
	OctP bias	V	-18	-8	-20	-8	-25	-20
	KED	V	13	-20	-20	-20	-5	-20

Cool plasma conditions can be used successfully for low concentration silicon sample analysis, delivering superior BEC and DL for several elements with low ionization potential. However cool plasma conditions accelerate silicon dioxide crystal deposition on the skimmer cone if used during the analysis of high concentration Si matrix samples. It is not recommended to use cool plasma when the Si concentration is higher than 50 ppm in the sample solution. In order to improve the detection of some elements, particularly Ca, in cool plasma mode, a small flow of hydrogen was added to the cell [1].

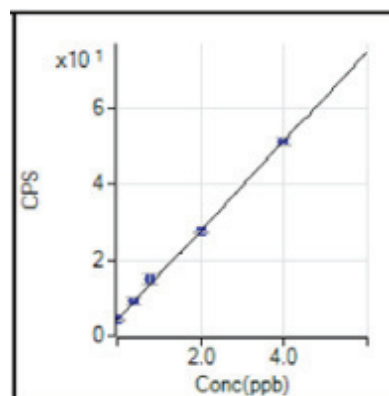
Analysis of high matrix samples, such as 2000 ppm Si solution, requires a robust tuning for best long-term stability. In addition to high plasma power, the lens setting can also be optimized for matrix tolerance by applying 0 volts to the first extraction lens. With a slight sacrifice of sensitivity, less signal suppression and better long term stability are obtained. Ion lens voltages except those in Table 1 were all optimized by the auto-tune function of the instrument.

Results

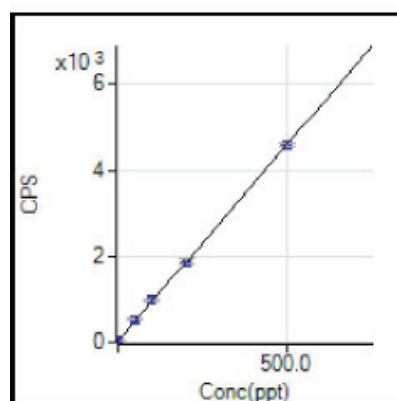
Calibration plots for the challenging elements P and Ti, measured in the optimum MS/MS mode in 2000 ppm Si sample, are given in Figure 1. P was measured in H₂ reaction mode (product ion PH₄⁺ at m/z 35), while Ti was measured in O₂ reaction mode (product ion TiO⁺ at m/z 64). P can also be measured in O₂ reaction mode (product ion PO⁺ at m/z 47). Preliminary tests showed that O₂ mode provided BEC of 5.86 ppb, while H₂ mode yielded a significantly lower BEC of 0.35 ppb.

In addition to the two difficult elements P and Ti discussed above, a full suite of elements of interest in the semiconductor industry was also measured in the Si matrix samples. Results for DL and BEC for all analytes are shown in Tables 2 and 3. These results were calculated from standard addition curves generated by spiking the multi-element standard into the 30 ppm and 2000 ppm Si matrix solutions. The acid concentration in all cases was 3.8% HF and 6.8% HNO₃. It is worth noting that a common scanning solution of VPD

contains 2% HF and 2% H₂O₂, but no HNO₃. However, this experiment required the use of HNO₃ with HF to dissolve the bulk Si wafer. Even after dilution in UPW, the final concentration of acid was several percent. It is well known that HNO₃ increases the background counts at mass 31 and accelerates SiO₂ deposition on the skimmer cone. Therefore, it should be noted that the experimental conditions applied here are more severe than actual VPD sample analysis.



31 -> 35 P [H2 MMS]
 $y = 1.182E1 x + 4.114E0$
 R 0.9995
 DL 0.2132
 BEC 0.3482



48 -> 64 Ti [O2 MMS]
 $y = 9.163E0 x + 2.540E1$
 R 0.9999
 DL 1.945
 BEC 2.772

Figure 1. Calibration curve of P (MS/MS; H₂ mode) and Ti (MS/MS; O₂ mode) in 2000 ppm Si sample

Table 2. DL and BEC of elements in 30 ppm Si solution (ppt except S, ppb)

Element	Mass	Tune	DL	BEC
Li	7	Cool	0.01	0.01
Be	9	No gas	0.93	0.18
B	11	No gas	11	29
Na	23	Cool	0.09	0.94
Mg	24	Cool	0.47	0.17
Al	27	Cool	1.7	0.63
P	31/35	H ₂	110	210
S	34/50	O ₂	2.1	34
K	39	Cool	1.0	1.7
Ca	40	Cool	3.0	1.1
Ti	48/64	O ₂	0.90	0.70
V	51/67	O ₂	0.34	1.7
Cr	52	Cool	1.7	0.72
Mn	55	Cool	0.01	0.01
Fe	56	Cool	1.9	1.2
Co	59	Cool	0.01	0.01
Ni	60	O ₂	1.0	1.0
Cu	63	O ₂	2.8	8.8
Zn	64	O ₂	5.2	19
Ga	71	Cool	0.01	0.01
Ge	74/90	O ₂	5.3	4.1
As	75/91	O ₂	4.5	12
Se	78/94	O ₂	6.2	6.3
Rb	85	Cool	0.36	0.90
Sr	88	Cool	0.01	0.01
Zr	90/106	O ₂	0.01	0.01
Nb	93/125	O ₂	0.40	0.08
Mo	98/130	O ₂	1.5	1.3
Ru	101	No gas	0.63	1.1
Rh	103	O ₂	0.64	8.1
Pd	105	O ₂	1.6	0.43
Ag	107	Cool	0.01	0.01
Cd	114	O ₂	0.01	0.01
Sn	118	O ₂	1.1	1.1
Sb	121	O ₂	0.79	0.33
Te	125	O ₂	2.4	0.80
Cs	133	Cool	0.01	0.01
Ba	138	O ₂	0.01	0.01
Hf	178/194	O ₂	0.01	0.01
Ta	181/213	O ₂	0.26	0.09
W	182/214	O ₂	1.8	0.50
Re	185	No gas	0.21	0.06
Ir	193	No gas	0.20	0.31
Pt	195	O ₂	1.6	1.2
Au	197	O ₂	0.45	0.09
Tl	205	No gas	0.36	0.21
Pb	208	Cool	0.01	0.01
Bi	209	No gas	0.04	0.01
Th	232/248	O ₂	0.01	0.01
U	238/254	O ₂	0.02	0.01

Table 3. DL and BEC of elements in 2000 ppm Si solution (ppt except S, ppb)

Element	Mass	Tune	DL	BEC
Li	7	No gas	0.87	0.39
Be	9	No gas	0.01	0.01
B	11	No gas	37	410
Na	23	H ₂	33	140
Mg	24	No gas	1.1	1.0
Al	27	H ₂	12	33
P	31/35	H ₂	210	350
S	34/50	O ₂	2.9	28
K	39	H ₂	26	240
Ca	40	H ₂	4.4	14
Ti	48/64	O ₂	2.0	2.5
V	51/67	O ₂	0.51	0.62
Cr	52	O ₂	9.2	100
Mn	55	H ₂	4.8	9.0
Fe	56	H ₂	16	240
Co	59	O ₂	0.84	1.7
Ni	60	O ₂	13	20
Cu	63	O ₂	5.9	14
Zn	64	O ₂	14	18
Ga	71	H ₂	3.1	3.7
Ge	74/90	O ₂	8.7	2.8
As	75/91	O ₂	4.6	5.0
Se	78/94	O ₂	8.4	7.2
Rb	85	No gas	14	19
Sr	88	H ₂	0.40	0.34
Zr	90/106	O ₂	0.58	0.19
Nb	93/125	O ₂	0.10	0.01
Mo	98/130	O ₂	2.7	0.78
Ru	101	No gas	3.7	4.1
Rh	103	H ₂	0.82	6.2
Pd	105	O ₂	0.70	0.25
Ag	107	No gas	0.94	0.74
Cd	114	O ₂	0.45	0.24
Sn	118	O ₂	2.9	7.2
Sb	121	O ₂	0.76	0.28
Te	125	O ₂	2.7	0.41
Cs	133	No gas	0.31	0.28
Ba	138	O ₂	0.41	0.09
Hf	178/194	O ₂	0.01	0.01
Ta	181/194	O ₂	0.01	0.01
W	182/214	O ₂	1.0	0.25
Re	185	No gas	0.23	0.03
Ir	193	No gas	0.34	0.18
Pt	195	No gas	1.8	0.77
Au	197	No gas	1.2	0.38
Tl	205	No gas	0.61	0.61
Pb	208	No gas	0.95	0.75
Bi	209	No gas	0.16	0.02
Th	232	No gas	0.01	0.01
U	238	No gas	0.01	0.01

Long term stability over three hours of continuous analysis was confirmed for 2000 ppm Si solution. In Figure 2, typical examples of phosphorus (4 ppb), sulfur (40 ppb) and titanium (500 ppt) signal plot are shown.

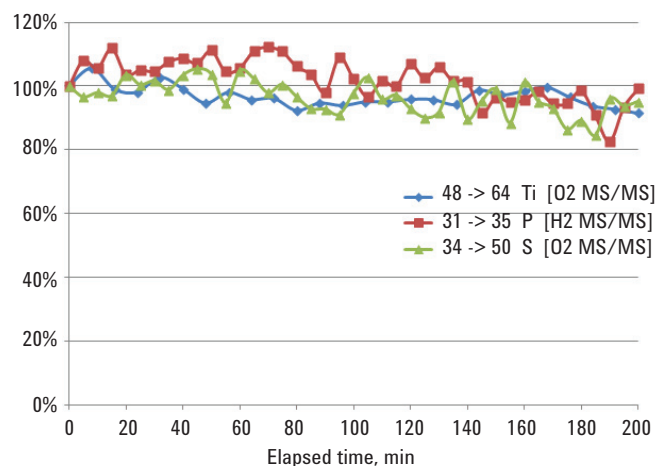


Figure 2. Three hour long-term stability test for 2000 ppm Si sample

Conclusions

MS/MS mode on the Agilent 8800 ICP-QQQ was shown to be very useful and effective for the determination of P, Ti, and other trace elements in high purity silicon matrices of different concentrations (30 ppm and 2000 ppm). Very low BECs and DLs could be realized for all elements, and MS/MS mode ensured reliable separation of the target product ions from potential overlapping product ions from other analytes. This capability is unique to MS/MS mode on the 8800 ICP-QQQ. Even by using an ultra low flow nebulizer, excellent sensitivity and low DLs were obtained, and good signal stability was demonstrated over a three hour testing period for the 2000 ppm Si sample.

References

1. Junichi Takahashi, Katsuo Mizobuchi and Masakazu Yukinari, 2008 Third Asia-Pacific Winter Conference on Plasma Spectrochemistry, page 34 of Book of Abstracts, Tsukuba, Japan.

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