Application Note

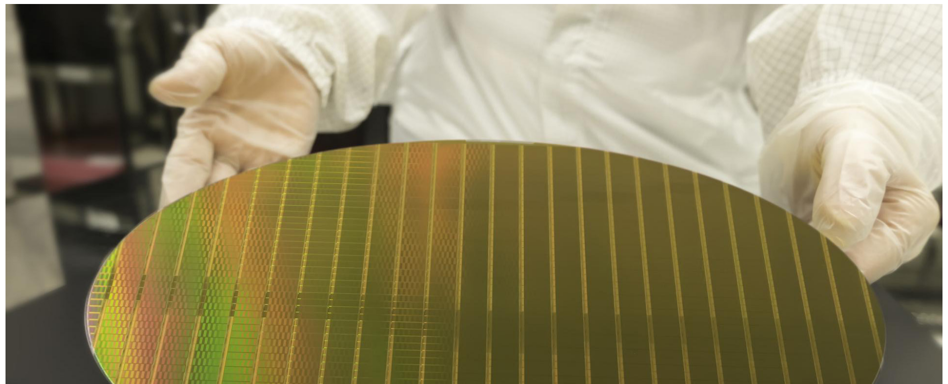
Semiconductor

Agilent

Trusted Answers

Analysis of Ultratrace Impurities in High Silicon Matrix Samples by ICP-QQQ

Determination of 38 elements in high matrix samples using an Agilent 8900 ICP-QQQ with optional m-lens



Authors

Yu Ying
Agilent Technologies
(China) Co., Ltd.

Introduction

Rapid developments in the emerging fields of artificial intelligence (AI) and the Internet of Things (IoT) are driving innovation in the integrated circuit (IC) sector of the semiconductor industry. IC fabrication plants (known as FABs or IC foundries) are increasing production of ICs to meet the requirements of this expanding market, as well as serving ongoing demand from other high-tech industries. Silicon (Si) is essential to the IC industry, as most modern electronics are based on Si semiconductors. These devices are made from millions of individual transistors (or switches) packed onto a Si wafer chip. Smaller transistors give higher core density, faster processing speed, lower power consumption, and less heat generation, critical factors for mobile devices. Currently, FABs are producing chips with transistor "gates" 10, 7, or even 5 nanometers (nm) long, with ongoing research projects to reduce the gate length even further. Manufacturing ICs at this small

scale and high density requires excellent control of the quality of the Si substrate and process chemicals. It is important that the performance of the analytical instruments used to detect metallic impurities in raw materials evolves to meet the needs of the semiconductor industry.

Single quadrupole ICP-MS is the most widely used atomic spectrometry technique for the measurement of trace elements in many semiconductor applications due to its sensitivity and multi-element capability (*1*). However, more advanced semiconductor processes require elemental impurities on the Si wafer to be less than 1.0×10^7 atom/cm^2 level. While it is difficult to meet these specifications using single quadrupole ICP-MS, triple quadrupole ICP-MS (ICP-QQQ) with MS/MS operation has further improved the sensitivity, background, and interference removal capabilities of the technique. With detection limits (DLs) for many elements at the sub-ppt level, ICP-QQQ is increasingly used in the semiconductor industry for the accurate analysis of the highest purity semiconductor materials (*1*).

Another challenge of measuring trace metal impurities in a high Si matrix by ICP-MS relate to physical effects arising from the matrix. The high levels of Si in the sample can lead to deposition of Si on the sampling cone and suppression of analytes, leading to instability and signal drift. Operating single quadrupole ICP-MS with a “cool” or reduced-energy plasma has been widely used in the semiconductor industry for many years for the analysis of high-purity chemicals and materials. Cool plasma suppresses the formation of intense argon-based interferences such as Ar^+ and ArO^+, allowing low-level analysis of ^{40}Ca and ^{56}Fe, respectively. A lower-temperature plasma also causes less re-ionization of traces of easily ionized elements (EIEs) from the cones and ion lens, giving lower background signals for these elements than normal plasma conditions. However, the lower power used with cool plasma conditions provides insufficient energy to decompose some sample matrices, including high Si matrix samples.

The Agilent 8900 ICP-QQQ fitted with an optional “m-lens” ion lens uses normal plasma conditions to analyze silicon-rich samples. The m-lens has an optimized geometry that minimizes background signals from EIEs deposited on the ICP-MS interface components. The 8900 with m-lens provides ppt-level background equivalent concentrations (BECs) for the elements of interest in the semiconductor industry, including the easily-ionized alkaline elements. The low BECs enable the monitoring of ultra-trace ppt-level impurities in high Si matrices using high-power, robust, matrix tolerant plasma conditions.

In this study, the 8900 ICP-QQQ was used to analyze two Si samples prepared at matrix levels that are typically analyzed in the semiconductor industry. Excellent precision was achieved for the measurement of 50 ppt spikes in the Si matrix samples over a 1 hour analytical run, demonstrating the effectiveness, robustness, and sensitivity of the method.

Experimental

Reagents

All samples and standards were prepared in semiconductor grade TAMAPURE AA-100 nitric acid (HNO_3) and hydrofluoric acid (HF) bought from Tama Chemicals Co. Ltd, Kanagawa, Japan. The ultrapure water (UPW) was supplied from Organo Corp (Tokyo, Japan).

Sample preparation

Pieces of electronic grade (9N purity) poly-silicon were weighed to the nearest 0.05 g and the sample surfaces were cleaned with HNO_3 and rinsed with UPW. To prepare a 1000 ppm Si matrix solution, the Si pieces were digested in a 1:1 (w/w) acid mix of 38% HF and 55% HNO_3. The Si matrix solution was then diluted to provide two typical Si matrix samples. A 10 ppm Si solution was used to represent the Si matrix level in a sample prepared by scanning the wafer using a vapor phase decomposition (VPD) device. A 100 ppm Si matrix solution was used to represent the matrix level that would be present in a digested poly-silicon sample.

Calibration standards

Simple, aqueous (no Si matrix) calibration standards were prepared in the same acid concentration as the 10 and 100 ppm Si samples using Agilent stock solutions. Multi-element calibration standards included “2A” (p/n 8500-6940) and “4” (p/n 8500-6942). Single element standards at 1000 µg/mL were used for antimony (p/n 5190-8562) and tin (p/n 5190-8583).

A multi-element spike solution containing all elements was also prepared from the stock solutions. The spike solution was added to the 10 and 100 ppm Si matrix samples at 50 ng/L (ppt).

Instrumentation

An Agilent 8900 ICP-QQQ was used for the analysis. The 8900 was fitted with an inert (HF-resistant) sample introduction system comprising a 200 µL/min MicroFlow PFA nebulizer, a PFA spray chamber, endcap, and connector tube, and a demountable torch with a 2.5 mm internal diameter (i.d.) sapphire injector. A Pt-tipped sampling cone was used, together with the optional m-lens (G3666-67500), and Pt-tipped, Ni-based skimmer cone for m-lens (G3666-67501).

The PFA nebulizer and Pt tipped sampling cone are standard on the 8900 #200 (Semiconductor Applications model). The other sample introduction parts (PFA spray chamber, endcap, connecting tube, and demountable torch) are included in the Inert Kit (G4912A #001). The sample introduction and interface parts listed are also compatible with the 8900 #100 (Advanced Applications model).

A high Si matrix leads to the formation of several polyatomic ions, which cause significant spectral interferences on some important elements such as Ti, Fe, Ni, Cu, and Ge (Table 1). To achieve the lowest BEC for each analyte in the silicon-rich samples, optimized ICP-QQQ acquisition conditions were used for different elements. Using ICP-MS MassHunter instrument control software, it is simple to measure different analytes in different cell gas modes using a single multitune method. During data acquisition, the ORS[4] cell gases and measurement modes are switched automatically, giving a fast and automated analysis using the best mode for each analyte.

In this study, several reaction cell gases (He, H_2, O_2, and NH_3) were used as appropriate for the large number of analytes being measured. Details of the configuration and principles of ICP-QQQ and MS/MS are explained elsewhere (*2, 3*). The operating parameters of the 8900 ICP-QQQ are given in Table 2.

Results and discussion

Background equivalent concentrations

The blank, 10 ppm, and 100 ppm Si samples were measured by external calibration method and the BECs of each sample were calculated using ICP-MS MassHunter. The BECs of all 38 analytes were lower than 50 ng/L in both the 10 and 100 ppm Si matrix blank samples, with most below 5 ng/L (Table 3). The low BECs show the effectiveness of the ICP-QQQ method at removing interferences on all analytes, including Si-based interferences on Ti, Fe, Ni, Cu, and Ge (Table 1). The relatively high BECs for some analytes may be due to the contamination during sample preparation.

Spike-recovery and stability test

The stability, robustness, and matrix tolerance of the instrument and method were tested over an hour of continual measurements. The unspiked (blank) Si samples were measured three times and each spiked sample was measured 11 times over the 60 minute run. The average recoveries of the 50 ng/L spikes ranged from 90 to 110% for all elements apart from Fe at 112% in the 10 ppm Si sample (Table 3). The slightly higher recovery of Fe was likely due to sample contamination from the laboratory environment. The 8900 ICP-QQQ also provided excellent sensitivity and accuracy for all elements, including EIEs, as shown by the spike recoveries in both Si matrices.

The relative standard deviation (RSD) of the measurements (n=11) was <6% for all 38 elements in both Si matrices, indicating minimal signal drift during the run using the 8900 with m-lens. Figure 1 shows the stability test results of some typical elements of importance to IC foundries such as Fe in the 100 ppm Si matrix sample.

Table 1. Potential spectral interferences in a Si matrix digest with HF.

Analyte Ion	Interference
$^{46}Ti^+$	$^{30}Si^{16}O^+$
$^{47}Ti^+$	$^{28}Si^{19}F^+$ $^{30}Si^{16}OH^+$
$^{48}Ti^+$	$^{29}Si^{19}F^+$ $^{30}Si^{18}O^+$
$^{49}Ti^+$	$^{30}Si^{19}F^+$
$^{58}Ni^+$	$^{28}Si^{30}Si^+$ $^{29}Si^{29}Si^+$
$^{60}Ni^+$	$^{28}Si^{16}O_2^+$ $^{30}Si^{30}Si^+$

Analyte Ion	Interference
$^{56}Fe^+$	$^{28}Si^{28}Si^+$
$^{63}Cu^+$	$^{28}Si^{16}O^{19}F^+$
$^{65}Cu^+$	$^{30}Si^{16}O^{19}F^+$ $^{28}Si^{18}O^{19}F^+$
$^{72}Ge^+$	$^{28}Si^{28}Si^{16}O$
$^{74}Ge^+$	$^{28}Si^{28}Si^{18}O$ $^{30}Si^{28}Si^{16}O$

Table 2. ICP-QQQ operating conditions.

	No Gas	H_2	NH_3	He
Acquisition Parameters				
Scan Mode	MS/MS			
Stabilization Time (s)	15	25	25	20
Replicates	3			
Sweeps/Replicate	100			
Integration Time (s)	0.6			
Plasma				
RF Power (W)	1550			
Sampling Depth (mm)	8.0			
Carrier Gas (L/min)	0.8			
Makeup Gas (L/min)	0.4			
Lenses				
Extract 1 (V)	1.5			
Extract 2 (V)	−70			
Omega Bias	−20			
Omega Lens	6			
Cell				
He Flow Rate (mL/min)				4.0
H_2 Flow Rate (mL/min)		10.0		
*NH_3 Flow Rate (mL/min)			2.0	
Octopole Bias (V)	−8	−18	−6	−20
Axial Acceleration (V)	0	1	1.5	0
KED (V)	3	−8	−10	5

*Mix of 10% NH_3 in 90% He

Table 3. Analysis results of 10 and 100 ppm Si matrix samples and matrix-spiked samples, n = 11.

			10 ppm Si Matrix Sample			100 ppm Si Matrix Sample		
Element	Q1/Q2	Cell Gas	BEC (ng/L)	%RSD of 50 ppt-Spiked Samples	50 ppt Spike Recovery Average (%)	BEC (ng/L)	%RSD of 50 ppt-Spiked Samples	50 ppt Spike Recovery Average (%)
Li	7/7	No gas	0.38	3.7	101.4	0.60	3.4	107.3
Be	9/9	No gas	0.00	3.6	99.4	0.87	4.7	105.7
B	11/11	No gas	16.1	4.0	105.9	30.2	3.2	109.7
Na	23/23	H_2	5.13	5.6	101.8	13.3	2.9	96.7
Mg	24/24	H_2	1.45	3.0	93.9	5.82	4.4	108.2
Al	27/27	H_2	8.52	3.8	103.1	46.6	2.6	97.7
K	39/39	H_2	10.8	2.3	93.6	10.3	2.6	105.1
Ca	40/40	H_2	7.99	2.1	95.8	7.79	3.3	108.9
Ti	48/114	NH_3	5.35	5.4	101.3	4.55	5.4	101.7
V	51/67	NH_3	0.00	2.5	90.8	0.30	4.6	102.3
Cr	52/52	NH_3	4.30	2.5	95.9	9.71	2.8	101.4
Mn	55/55	NH_3	35.7	3.8	103.8	43.3	1.5	96.2
Fe	56/56	H_2	21.6	6.0	112.0	23.6	3.9	106.9
Ni	58/58	NH_3	6.75	2.4	90.0	4.69	3.2	99.1
Co	59/59	NH_3	2.37	4.0	92.2	5.56	2.3	96.7
Zn	64/64	NH_3	1.92	5.6	99.4	34.8	5.9	94.5
Cu	65/65	NH_3	4.19	5.1	101.1	33.6	5.7	95.7
Ga	69/69	H_2	0.34	2.4	94.8	6.13	2.8	109.8
Ge	74/74	H_2	4.26	2.0	90.7	4.30	1.7	98.1
As	75/75	H_2	0.86	4.7	90.3	0.29	5.9	100.4
Se	78/78	H_2	1.24	5.0	90.4	1.60	4.5	97.2
Rb	85/85	H_2	0.62	2.0	96.5	18.4	4.5	100.6
Sr	88/88	H_2	0.02	2.0	95.3	0.03	2.5	101.2
Zr	90/90	H_2	0.08	1.9	94.9	0.03	2.3	102.2
Nb	93/93	He	0.43	2.6	91.5	0.12	2.7	98.2
Mo	95/95	He	0.12	2.9	93.8	0.53	4.3	98.0
Ag	107/107	No gas	0.12	1.9	98.2	0.18	1.6	100.8
Cd	114/114	NH_3	0.02	1.7	95.9	0.00	2.5	98.1
Sn	118/118	NH_3	0.51	2.5	96.7	1.12	2.1	97.6
Sb	121/121	NH_3	0.14	2.3	93.9	0.24	2.6	95.3
Cs	133/133	He	0.03	2.7	94.6	0.03	1.8	97.0
Ba	138/138	H_2	0.42	2.3	97.6	0.43	1.9	98.4
Ta	181/181	He	0.17	2.2	98.8	0.09	1.6	96.4
W	182/182	He	3.48	4.2	99.2	0.12	2.2	96.1
Re	185/185	He	0.00	2.9	95.8	0.01	1.9	95.9
Tl	205/205	No gas	0.15	3.0	104.2	0.12	1.3	103.2
Pb	208/208	NH_3	0.31	2.2	98.0	0.19	1.9	96.1
U	238/238	No gas	0.00	3.3	103.2	0.00	1.0	101.2

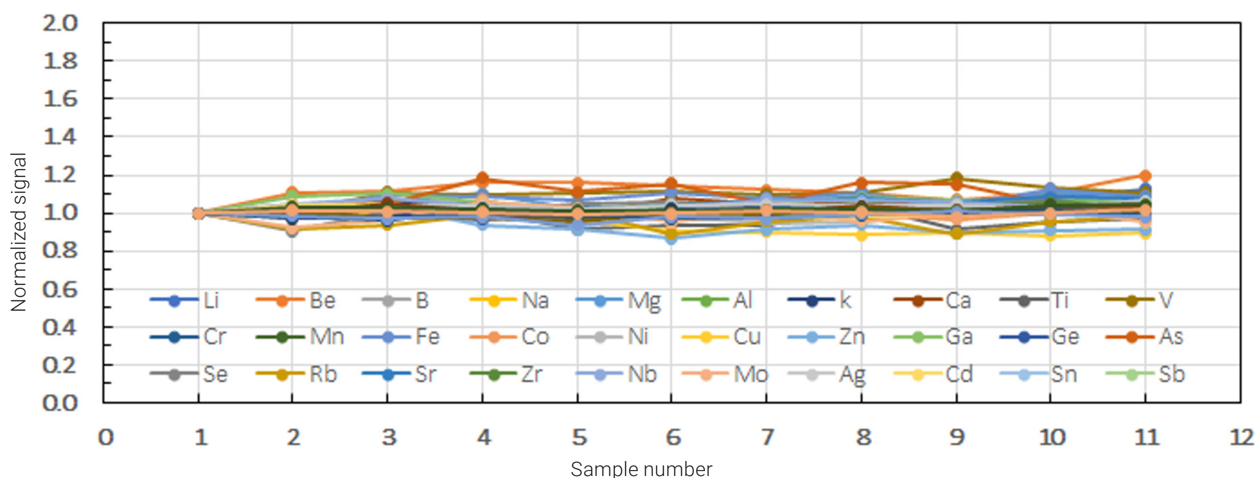


Figure 1. Stability results for multiple elements spiked at 50 ppt in a 100 ppm Si matrix sample.

Conclusion

The robustness of the Agilent 8900 ICP-QQQ with m-lens was demonstrated for the determination of 38 elements in two digested silicon samples containing 10 and 100 ppm Si. The optional m-lens ensured that the background signals for the EIEs were minimized, allowing all elements to be measured at ppt levels using matrix tolerant, high-power plasma conditions.

The best BECs for all elements were achieved by operating the 8900 ICP-QQQ in MS/MS mode using a single multitune method with different cell gases. The low BECs showed that the method successfully removed all spectral interferences, including Si-based interferences on Ti, Fe, Ni, Cu, and Ge.

The reproducibility (stability) results for the 50 ppt spikes in the two high silicon samples were between 1 and 6% RSD for all elements in a sequence lasting 1 hour. These results showed that there was minimal signal suppression or drift caused by Si deposition on the interface under the robust plasma conditions.

The study demonstrates the suitability of the 8900 ICP-QQQ for the characterization of trace metals in silicon-matrix samples. The method has the potential to meet the evolving needs and future specifications of the most advanced manufacturing processes that are required to meet the demand for higher IC performance.

References

1. Applications of ICP-MS: Measuring Inorganic Impurities in Semiconductor Manufacturing, Agilent publication, 5991-9495EN
2. Eduardo Bolea-Fernandez, Lieve Balcaen, Martin Resano, Frank Vanhaecke. Overcoming spectral overlap via inductively coupled plasma-tandem mass spectrometry (ICP-MS/MS). A tutorial review, *J. Anal. At. Spectrom.*, **2017**, 32, 1660–1679
3. Ed McCurdy, Glenn Woods, Naoki Sugiyama. Method Development with ICP-MS/MS: Tools and Techniques to Ensure Accurate Results in Reaction Mode, *Spectroscopy*, **2019** (9):20–27, http://www.spectroscopyonline.com/method-development-icp-msms-tools-and-techniques-ensure-accurate-results-reaction-mode

www.agilent.com/chem

DE44166.9420717593

This information is subject to change without notice.

© Agilent Technologies, Inc. 2021

Printed in the USA, January 26, 2021
5994-2890EN

Agilent
Trusted Answers