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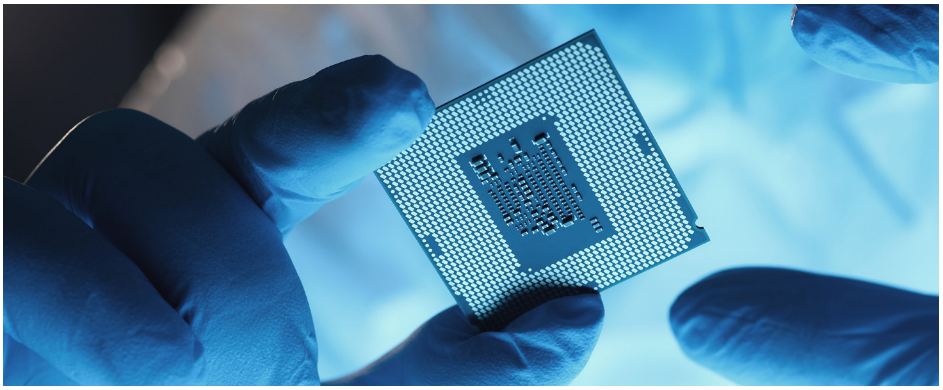
Trace Elemental Analysis of Precursor Materials Using ICP-MS/MS

Robust detection of Pt, Ag, Cd, and Ti in high-metal matrices using the Agilent 8900 ICP-QQQ and reactive cell gases



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Introduction

Precursor materials are fundamental to the fabrication of integrated circuits (ICs). In atomic layer deposition (ALD), they enable the controlled growth of ultrathin films on semiconductor substrates—an essential capability for scaling advanced device architectures. Because even trace metal impurities in precursors can degrade film performance and device yield, both suppliers and manufacturers routinely analyze these materials. Due to its sensitivity and multi-elemental capabilities, inductively coupled plasma mass spectrometry (ICP-MS) is the industry standard for assessing elemental impurities in semiconductor materials.[1] However, the high concentration of the metallic (high-matrix) content of precursors and the prevalence of polyatomic and doubly charged ion (M^{++}) spectral overlaps arising from the matrix on key analytes present challenges for accurate analysis by single-quadrupole ICP-MS. At one time, high-resolution (HR)-ICP-MS (m/Δm up to 10000) was the best choice for solving these kinds of analytical problems. But some interferences require a resolution that exceeds the capability of current HR-ICP-MS instruments. In these cases, the samples are sometimes diluted to reduce the concentration of matrix elements, but dilution cannot totally solve the interference and may negatively affect detection limits.

Triple quadrupole ICP-MS (ICP-QQQ or ICP-MS/MS) combined with collision/reaction (CRC) gases overcomes these limitations by selectively removing or avoiding interferences without compromising sensitivity. Agilent ICP-QQQ systems use two quadrupoles (Q1 and Q2) as unit mass filters, enabling MS/MS operation and the controlled use of reactive cell gases. Q1 controls which ions enter the CRC and Q2 controls which ions reach the detector.[2–4]

In this study, we evaluated the performance of the Agilent 8900 ICP-QQQ to determine key analytes in three simulated precursor materials. Each sample contained a high-concentration matrix of hafnium (Hf), zirconium (Zr), or molybdenum (Mo), which cause interferences on platinum (Pt), silver (Ag), and cadmium (Cd) and titanium (Ti), respectively. To demonstrate the 8900 ICP-QQQ system's ability to remove spectral interferences without sacrificing sensitivity, we quantified the four analytes in the three matrices using optimized instrument operating conditions.

Experimental

Preparation of simulated precursor materials and calibration standards

All acids used in this study were sourced from Kanto-PPC Inc. and BASF in Taiwan. Samples and standards were prepared in precleaned perfluoroalkoxy (PFA) vials. The vials had been soaked in diluted hydrofluoric acid (HF) and nitric acid (HNO_3), then rinsed with ultrapure water (UPW).

To prepare the Hf and Zr matrix samples at 500 ppm, Agilent 10,000 ppm standard solutions of each element were diluted with 2% hydrochloric acid (HCl). Calibration standards for Pt and Ag were prepared by diluting Agilent standards with 2% HCl.

A $MoCl_5$ solution prepared using HF and HNO_3 was supplied. The final concentration of the Mo matrix level was 360 ppm, as measured by an Agilent 5800 ICP-OES. Calibration standards for Cd and Ti were prepared by diluting Agilent standards with 2% HNO_3.

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ (#200) fitted with the optional m-lens was used for all measurements. The 8900 #200 includes 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 (id) sapphire injector. The cones comprised a Pt-tipped sampling cone and Pt-tipped, Ni-based skimmer cone for m-lens. The samples were self-aspirated using an Agilent SPS 4 autosampler. Hot plasma conditions (<1% CeO^+/Ce^+) were used during the analysis of the high-matrix samples.

The 8900 ICP-QQQ was operated in MS/MS mode for all measurements. Ammonia (NH_3) —plus a flow of helium (He) as a buffer gas—and oxygen (O_2) were used as reactive cell gases to resolve the matrix-based interferences. Various CRC tuning modes and Q1–Q2 mass setting combinations were tested to obtain the best conditions for each analyte. The optimized operating conditions for the analysis are detailed in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating conditions optimized for the determination of the target elements in the various matrices.

Analyte	Pt	Ag	Cd	Ti
Major Matrix Element	Hf	Zr	Mo	
RF Power (W)	1500			
Sampling Depth (mm)	6		8	
Nebulizer Gas Flow Rate (L/min)	0.70		0.65	
Makeup Gas Flow Rate (L/min)	0.38		0.55	0.45
Cell Gas and Flow Rate (mL/min)	He, 1.0			O_2, 0.38 (25%)
	*NH_3, 3.5 (35%)		*NH_3, 2.7 (27%)	
Axial Acceleration (V)	1.5		2.0	1.5
Energy Discrimination (V)	−8		−10	−7

*NH_3 cell gas comprised a 50:50 mix of NH_3 and He

Results and discussion

Pt analysis in a 500 ppm Hf matrix

A high Hf matrix leads to the formation of HfO^+ and $HfOH^+$ polyatomic ions, which potentially cause significant spectral interferences on all six of the naturally occurring isotopes of Pt (Table 2). Theoretically, the Pt-198 isotope should yield the most reliable data because it combines the lowest calculated interference ratios for HfO^+ and $HfOH^+$ with a relatively high natural abundance.

Table 2. Theoretical Hf-based interferences on the six naturally Pt occurring isotopes.

Pt Isotope Mass Number	Pt Natural Abundance (%)	HfO^+ Interference Ratio (%)	$HfOH^+$ Interference Ratio (%)
190	0.01	0.16	0.00
191		0.00	0.16
192	0.78	5.25	0.00
193		18.56	5.25
194	32.86	27.22	18.55
195	33.78	13.64	27.23
196	25.21	35.06	13.63
197		0.04	35.05
198	7.36	0.07	0.04

An ICP-MS/MS "mass-shift" method was used for the determination of Pt at ultratrace concentrations in a 500 ppm Hf matrix. NH_3 gas reacted readily with Pt ions in the cell to form a reaction product ion, $Pt(NH_3)_2^+$. Since NH_3 did not react with the Hf-based polyatomic interferences, HfO^+ and $HfOH^+$, this method enabled the analyte to be measured at the product ion mass at M + 34 u. For example, setting Q1 to 198 and Q2 to 232, effectively shifted Pt away from any interfering ions at *m/z* 198.

Pt calibration curves were generated using standards that did not contain a Hf matrix. Figure 1 shows the calibration curves for the four most abundant Pt isotopes, measured as $Pt(NH_3)_2^+$ reaction product ions at M + 34 u.

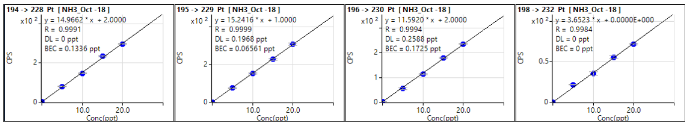

Figure 1. Pt calibration curves (non-matrix matched).

The quantitative results for the four most abundant Pt isotopes measured in the 500 ppm Hf matrix ranged from 2 ppt for ^{198}Pt to 334 ppt for ^{196}Pt (Table 3). These findings support the theoretical selection of ^{198}Pt as the most suitable isotope for this application, with NH_3 cell gas enabling interference-free detection at trace levels. The elevated concentrations for the other isotopes suggest residual signal contributions from HfO^+ and $HfOH^+$.

Table 3. Quantitative results for Pt in 500 ppm Hf determined using the Agilent 8900 ICP-QQQ in NH_3 mass-shift mode, measured as $Pt(NH_3)_2$.

	Q1 194 → Q2 228	Q1 195 → Q2 229	Q1 196 → Q2 230	Q1 198 → Q2 232
Measurement Result of Pt (ppt)	217	172	334	2.0

Ag analysis in a 500 ppm Zr matrix

As shown in Table 4, both naturally occurring Ag isotopes are affected by Zr-based interferences. ZrO^+ and $ZrOH^+$ appear in the mass spectrum between *m/z* 106 and 115, interfering with Ag at masses 107 and 109.

Table 4. Theoretical Zr-based interferences on the two naturally occurring Ag isotopes, ^{107}Ag and ^{109}Ag.

Mass Number	Ag Natural Abundance (%)	ZrO^+ Interference Ratio (%)	$ZrOH^+$ Interference Ratio (%)
107	51.84	11.21	51.33
108		17.22	11.21
109	48.16	0.03	17.22

As shown in Figure 2, NH_3 cell gas reacted readily with the Zr-based interferences in the CRC forming $Zr–NH_3$ reaction product ions that appear in the mass spectrum between *m/z* 140 and 144. This method effectively shifted the interferences to these higher masses, freeing the two Ag isotopes from interference and enabling them to measured on-mass at *m/z* 107 and 109.

Figure 2. Removal of Zr matrix-based interferences on $^{107}Ag^+$ and $^{109}Ag^+$ using the Agilent 8900 ICP-QQQ operating in NH_3 on-mass mode. The interfering ions (ZrO^+ and $ZrOH^+$) form reaction product ions which can be seen in the mass spectrum between 140 and 144 u, leaving the analyte ions free of interferences.

The results presented in Table 5 demonstrate the accuracy of the quantitative data for Ag in a 500 ppm Zr matrix. The concentration results for the two Ag isotopes are in good agreement and the signal ratio at 107:109 of 1.12 is similar to the natural isotope ratio of Ag (1.08). Also, there were only three counts per second (cps) at *m/z* 108, evidence that the ZrO^+ and $ZrOH^+$ interferences had been successfully shifted to higher masses.

Table 5. Quantitative results for Ag in a 500 ppm Zr determined using the Agilent 8900 ICP-QQQ in NH_3 on-mass mode, measured as $^{107}Ag^+$ and $^{109}Ag^+$.

	Q1 107 → Q2 107	Q1 108 → Q2 108	Q1 109 → Q2 109
Quantitative Result of Ag (ppt)	0.163	-	0.147
Counts per Second (cps)	347	3	310

Cd and Ti analysis in a 360 ppm Mo matrix

As shown in Tables 6 and 7, most Cd isotopes and all Ti isotopes are subject to polyatomic ion interferences arising from the high Mo matrix. Also, ^{106}Cd is overlapped by palladium (^{106}Pd), impeding its use. While ^{106}Cd was not measured in this study, the 8900 can resolve isobaric ion interferences, where isotopes of two different elements occur at the same mass, using an appropriate reactive cell gas method.[6]

Table 6. Theoretical Mo-based interferences on most naturally occurring Cd isotopes and an isobaric interference on ^{106}Cd.

Cd Isotope Mass Number	Cd Natural Abundance (%)	MoO^+ Interference Ratio (%)	$MoOH^+$ Interference Ratio (%)	Isobaric Interference
106	1.25			Pd-106
108	0.89	14.50		
110	12.49	9.16	14.50	
111	12.80	15.81	9.16	
112	24.13	16.65	15.81	
113	12.22	9.62	16.65	
114	28.73	24.37	9.62	
115	7.49	0.03	24.37	

Table 7. Theoretical Mo^{++} interferences on all naturally occurring Ti isotopes.

Ti Isotope Mass Number	Ti Natural Abundance (%)	Mo^{++} Interference Ratio (%)
46	8.25	14.53
47	7.44	9.15
48	73.72	16.67
49	5.41	24.39
50	5.18	9.82

Quantitative results and spike stability

The 8900 ICP-QQQ operating in NH_3 on-mass mode removes MoO^+ and $MoOH^+$ from Cd^+, since MoO/MoOH react with NH_3 to form ammonia cluster ions more readily than Cd. The agreement between the quantitative results for ^{111}Cd and ^{114}Cd of 0.9 and 0.6 ppt, respectively, confirm the effectiveness of the method (Table 8).

The results for Ti^+ demonstrate the interference removal capability of O_2 cell gas mode to handle Mo^{++} ion overlaps, as shown by the low single-digit ppt range results (Table 8). O_2 reacts with Ti to form TiO^+, mass-shifting it by 16 u. For example, ^{48}Ti is shifted from *m/z* 48 → 64, clear of the interference from $^{96}Mo^{++}$ at *m/z* 64. The consistency between the mass pairs 47 → 63 and 48 → 64 data further confirms the reliability of the O_2 mass-shift method for eliminating Mo^{++} interferences.

Table 8 also includes results from seven repeated measurements of Mo matrix samples spiked at 50 ppt with Cd and Ti. The %RSDs were ≤8%, indicating that the 8900 effectively removes interferences while maintaining stable performance under high-matrix conditions.

Table 8. Quantitative data for Cd and Ti in a 360 ppm Mo matrix determined using the Agilent 8900 ICP-QQQ using NH_3 on-mass and O_2 mass-shift mode, respectively, and precision of seven measurements of a spiked sample.

Analyte	Cell Gas Mode	Q1–Q2	Analyte Concentration (ppt)	Average Spike Concentration, n=7 (ppt)	RSD (%)
Cd	NH_3	111–111	0.9	45.2	5
Cd	NH_3	114–114	0.6	46.2	2
Ti	O_2	47–63	2.8	44.2	8
Ti	O_2	48–64	3.1	46.3	4

Conclusion

The Agilent 8900 Semiconductor configuration ICP-QQQ was evaluated for its ability to eliminate spectral interferences on four analytes—Pt, Ag, Cd, and Ti—in simulated semiconductor precursor materials using MS/MS and reactive cell gases. To accommodate challenging samples comprising Hf (500 ppm), Zr (500 ppm), and Mo (360 ppm) under hot plasma conditions (<1% CeO^+/Ce^+), the 8900 was equipped with the optional m-lens.

Ammonia was applied in both on-mass and mass-shift modes to quantify Pt, Ag, and Cd at single-digit or sub-ppt levels. Oxygen on-mass mode effectively removed Mo-based doubly charged ion interferences on Ti, enabling accurate detection at single-digit ppt concentrations. Repeated analysis of the $MoCl_5$ samples spiked at 50 ppt with %RSDs below 10% demonstrated the instrument's robustness and consistent performance for ultratrace quantification in complex matrices.

The 8900 ICP-QQQ delivered low background, high sensitivity, and reliable interference control, making it suitable for method development and trace-level screening of semiconductor materials.

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Products used in this application

Agilent products

MicroFlow inert PFA nebulizer

PFA inert sample introduction kit with 2.5 mm id platinum injector

ICP-MS sampler cone, platinum-tip with copper base

Pt (Ni base) skimmer for m-lens

Extraction-Omega lens assembly for m-lens of 8900

Hafnium (Hf) standard

Zirconium (Zr) standard

Multi-element calibration standard 2A, 10 mg/L

Multi-element calibration standard 3, 10 µg/mL

Multi-element calibration standard 4, 10 µg/mL

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DE-011006

Published in the USA, November 28, 2025
5994-8841EN

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