Application Note
Semiconductor

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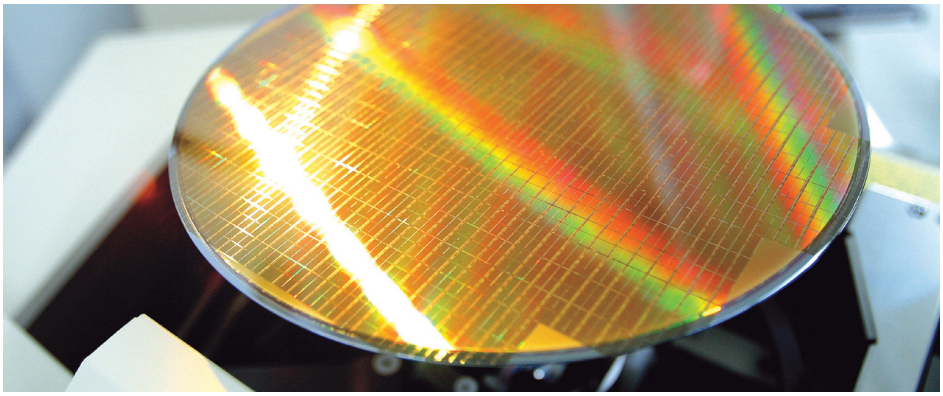
Ultrapure Process Chemicals Analysis by ICP-QQQ with Hot Plasma Conditions

Meeting single- and sub-ppt guideline levels for ASTM/SEMI elements in ultrapure water using an Agilent 8900 ICP-QQQ



Authors

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Introduction

Contamination control is critical in semiconductor device fabrication (FAB) facilities (*1*). Contaminants may be introduced via the wafer substrate, or the chemicals and reagents used during the manufacturing process. Impurities—particularly metal ions and particles – adversely affect device performance and production yield, so FABs use the highest purity reagents and follow strict protocols to control contaminants during the manufacturing process. Ultrapure water (UPW) is used throughout the wafer fabrication process including in the RCA standard cleaning (SC-1/SC-2) procedure to remove chemical contaminants and particulate impurities from the wafer surface. UPW is one of the most critical process chemicals for contamination-control as the water is in direct contact with the wafer surface at many stages of manufacturing. Any impurities present in the UPW could directly affect the electrical properties of the finished device, for example, by reducing dielectric breakdown voltage.

ASTM International and Semiconductor Equipment and Materials International (SEMI) publish standards regarding the specifications for semiconductor process chemicals and reagents, including UPW. ASTM D5127-13, 2018 and SEMI F63-0521, 2021 provide guidance for the quality of UPW needed to produce devices with linewidths < 0.045 microns (*2, 3*). Both standards require detection limits (DLs) of less than 0.5 ppt (boron has a higher limit of 15 ppt) and background equivalent concentrations (BECs) less than 1 ppt (50 ppt for B). The semiconductor industry standard method for monitoring trace element contaminants is ICP-MS, with laboratories increasingly switching to triple quadrupole ICP-MS (ICP-QQQ or ICP-MS/MS) for its superior detection limits. The Agilent 8900 ICP-QQQ is a tandem MS instrument, which uses MS/MS operation to further improve the performance of the technique compared to single quadrupole ICP-MS instruments.

The 8900 ICP-QQQ meets the electronic and semiconductor industry's need for trace and ultratrace element analysis due to its high sensitivity, low background, and interference removal capabilities. The 8900 has the flexibility to operate in several modes to give optimum performance across different applications. For example, semiconductor labs often use cool plasma conditions to achieve the lowest BECs and DLs for interfered elements and easily ionized elements (EIEs). Cool plasma reduces EIE backgrounds and suppresses the formation of intense argon-based interferences such as Ar^+, ArH^+, and ArO^+, allowing low-level analysis of ^{40}Ca, ^{39}K, and ^{56}Fe, respectively.

Cool plasma gives excellent results in low matrix samples, such as UPW, H_2O_2, HNO_3, and HCl (*4*). However, high matrix samples, such as silicon and metal digests, are difficult to run using cool plasma due to the higher level of matrix suppression. More robust, hot plasma (low CeO/Ce ratio) conditions are preferred for such sample types. For labs wishing to use only hot plasma, the 8900 ICP-QQQ can be fitted with an optional skimmer cone and m-lens that provide optimum performance in hot plasma conditions. In a recent study, an 8900 fitted with the optional m-lens was used to determine 38 elements in two digested silicon samples prepared at 10 and 100 ppm Si (*5*). The m-lens and the skimmer cone that it is paired with have an optimized geometry that minimizes EIE backgrounds when using normal, hot plasma conditions. Using m-lens, the 8900 was able to measure all required elements at ppt levels in the Si matrix without using cool plasma.

The 8900 with m-lens can also be used to analyze ultratrace elements in low matrix semiconductor samples – such as UPW – using only normal, hot plasma conditions. In this study, hot plasma was combined with no gas mode and two cell gas modes to resolve spectral interferences, achieving single- or sub-ppt BECs and DLs for all analytes.

Experimental

Reagents and sample preparation

UPW (Organo Corp, Tokyo, Japan) was acidified to 0.1% with high purity 68% HNO_3 (TAMAPURE AA-100, Japan). Acidification ensures that elements are retained as soluble ions in solution, although adding acid can potentially contribute to the level of contamination.

Calibration standards

The 8900 ICP-QQQ was calibrated using the method of standard addition (MSA), as is typical for the analysis of high-purity semiconductor samples. A mixed multi-element standard (SPEX CertiPrep, NJ, US) was prepared and spiked into the UPW to give standard additions at 5, 10, 20, and 40 ppt.

Instrumentation

The 8900 Semiconductor Configuration ICP-QQQ was fitted with standard components including a PFA-100 MicroFlow nebulizer, quartz spray chamber, quartz torch with 2.5 mm injector, and Pt sampling cone. The standard s-lens was replaced with an optional m-lens (part number G3666- 67500) and optional Pt-tipped, Ni-based skimmer cone for m-lens (part number G3666-67501). The 8900 includes the ORS^4 collision/reaction cell (CRC) and two quadrupoles (Q1 and Q2), one either side of the CRC, enabling double mass selection (MS/MS). Q1 rejects all nontarget ions before they enter the cell, allowing only analyte ions and on-mass interference ions to pass to the cell. The analyte and interfering ions can then be separated using predictable, consistent, and reproducible reaction chemistry (*6, 7*). Q2 then ensures that only the analyte ions (on-mass mode) or analyte-product ions (mass-shift mode) pass to the detector, free of interferences.

Agilent ICP-MS MassHunter instrument control software for the 8900 provides simple method setup to measure analytes in different cell gas modes using a single multitune acquisition. In this analysis no gas mode, ammonia reaction mode (using a mixture of ammonia and hydrogen cell gases), and oxygen reaction mode were used to remove interferences using a combination of on-mass and mass-shift measurement. During data acquisition, the cell gases and measurement modes were switched automatically, giving a fast and automated analysis using the best mode for each analyte. Instrument acquisition and operating parameters are given in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating conditions.

	No Gas	NH_3+H_2	O_2
Acquisition Parameters			
Scan Mode	MS/MS		
Replicates (standards)	3		
Replicates (blank)	10		
Integration Time per Mass (s)	1.0		
Plasma			
RF Power (W)	1600		
Sampling Depth (mm)	8.0		
Nebulizer Gas (L/min)	0.70		
CeO^+/Ce^+ (%)	2		
Cell			
He Flow Rate (mL/min)	-	1	-
H_2 Flow Rate (mL/min)	-	2	-
*NH_3 Flow Rate (mL/min)	-	2.0 (20%)	-
O_2 Flow Rate	-	-	0.45 (30%)
KED (V)	3	−10	−7

**Mix of 10% NH_3 in 90% He*

Results and discussion

Calibration curves

Four representative MSA calibration curves for K, Ca, Fe, and Ni in UPW are shown in Figure 1. No background subtraction or blank correction was performed. The four analytes are representative of the EIEs (K), elements with severe background interferences (Ca), elements of particular importance for the semiconductor industry (Fe), and elements that could indicate contamination from the ICP-MS interface (Ni). All the SEMI element calibrations showed excellent linearity (r > 0.999) and low BECs. This performance confirms the high sensitivity of the 8900 and the effectiveness of the reaction cell method with m-lens to control elemental backgrounds and resolve interferences.

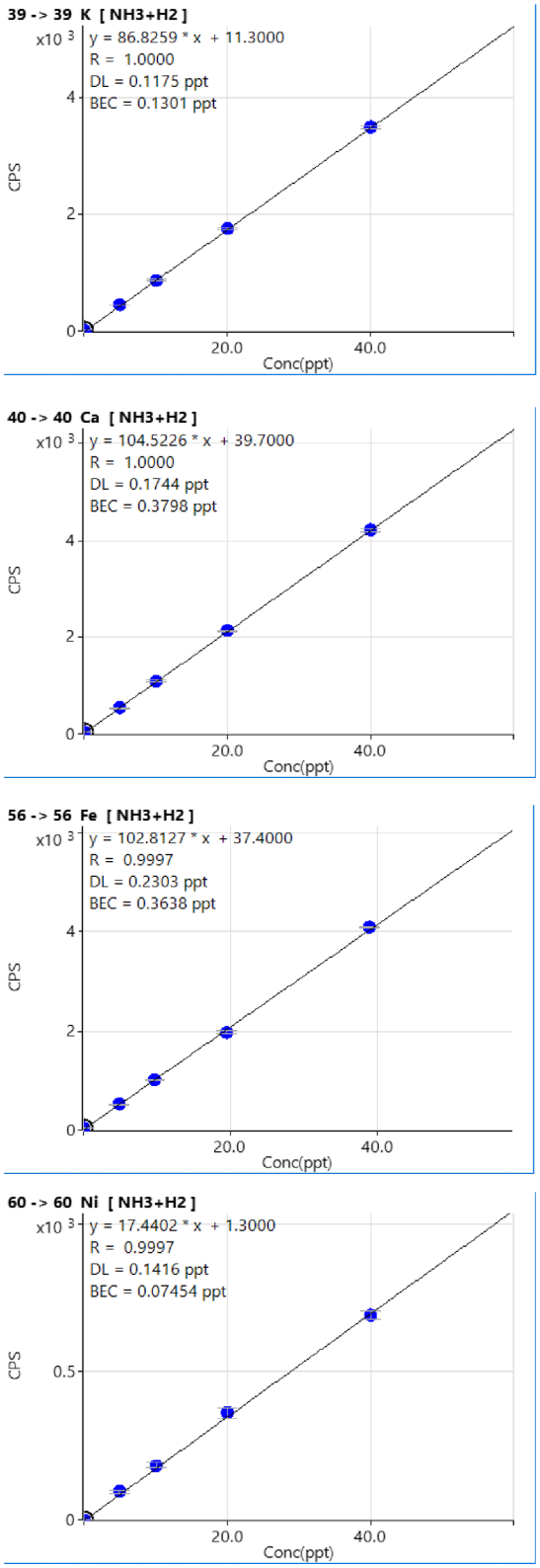

Figure 1. Representative MSA calibration plots for K, Ca, Fe, and Ni in UPW.

BECs and DLs

BECs and DLs for 26 elements were calculated automatically by the ICP-MS MassHunter software (Table 2). BECs below 0.5 ppt and DLs below 0.3 ppt were obtained for 25 SEMI elements, easily meeting the limits for UPW specified by ASTM and SEMI. The higher specified limits for boron (50 ppt BEC and DL of 15 ppt) were also easily achieved (measured BEC of 1.11 ppt and DL of 1.18 ppt). B backgrounds are highly dependent on water quality, but the BEC achieved in this work was a factor of 50 lower than the SEMI guideline, easily meeting current industry requirements. Critical metallic (conductive) contaminants such as Al, Cr, Fe, Co, Ni, Cu, Zn, and Mo were measured with BECs and DLs substantially below 0.5 ppt, again easily meeting industry requirements.

The results, which are also shown in Figure 2, demonstrate the suitability of the 8900 ICP-QQQ using hot plasma for the analysis of ultratrace contaminants in high purity semiconductor process chemicals.

Conclusion

The study has demonstrated the suitability of the Agilent 8900 ICP-QQQ with optional m-lens for the measurement of ultratrace-level contaminants in low-matrix semiconductor reagents such as UPW. The m-lens ensured that background signals for the EIEs – K, Na, Ba, and Li – were minimized, allowing all 26 SEMI-critical elements to be measured at ppt levels using hot plasma conditions (CeO/Ce ratio < 2%). All potential spectral interferences were resolved by operating the 8900 in MS/MS mode using a single multitune method with no gas and two reaction gas modes.

Standard addition calibration curves from 0 ppt to 40 ppt concentration range showed excellent linearity and sensitivity for all elements. The low BECs showed that the method successfully removed all spectral interferences, including argon-based interferences that typically form under hot plasma conditions. The 8900 method resolved the intense interferences such as Ar^+, ArH^+, and ArO^+, allowing sub-ppt analysis of ^{40}Ca, ^{39}K, and ^{56}Fe, respectively.

The BECs and DLs for all elements were well below the recommendations set by ASTM and SEMI for the quality of UPW related to semiconductor-industry manufacturing at < 0.045 m linewidths.

Table 2. Agilent 8900 ICP-QQQ DLs and BECs and ASTM/SEMI requirements for 26 elements in UPW.

				Measured in UPW by 8900		ASTM D5127-13 (2018) Requirements	SEMI F63-0521 (2021) Requirements	
Analyte	Tune Mode	Q1	Q2	DL (ppt)	BEC (ppt)	BEC (ppt)	BEC (ppt)	MDL (ppt)
Li	No gas	7		0	0	<1	<1	0.5
B	No gas	11		1.18	1.11	<50	<50	15
Na	No gas	23		0.26	0.23	<1	<1	0.5
Mg	NH_3+H_2	24		0.05	0.02	<1	<1	0.5
Al	NH_3+H_2	27		0.11	0.06	<1	<1	0.5
K	NH_3+H_2	39		0.12	0.13	<1	<1	0.5
Ca	NH_3+H_2	40		0.17	0.38	<1	<1	0.5
Ti	O_2	48	64	0	0	<10	<1	0.5
V	NH_3+H_2	51		0.04	0.01	<10	<1	0.5
Cr	NH_3+H_2	52		0.24	0.38	<1	<1	0.5
Mn	NH_3+H_2	55		0.08	0.09	<10	<1	0.5
Fe	NH_3+H_2	56		0.23	0.36	<1	<1	0.5
Co	NH_3+H_2	59		0.05	0.01	<1	<1	0.5
Ni	NH_3+H_2	60		0.14	0.07	<1	<3	1.6
Cu	NH_3+H_2	63		0.22	0.24	<1	<1	0.5
Zn	NH_3+H_2	64		0.15	0.06	<1	<1	0.5
As	O_2	75	91	0.23	0.02	<1	<1	0.5
Sr	NH_3+H_2	88		0.01	0.002	<1	<1	0.5
Mo	NH_3+H_2	98		0.04	0.01	<1	<1	0.5
Cd	NH_3+H_2	114		0.04	0.004	<10	<1	0.5
Sn	NH_3+H_2	118		0.12	0.03	<10	<1	0.5
Sb	NH_3+H_2	121		0.05	0.01	<1	<1	0.5
Ba	NH_3+H_2	138		0.03	0.003	<1	<1	0.5
W	O_2	184	216	0.20	0.30	<1	<1	0.5
Pt	O_2	195		0.20	0.40	<1	<1	0.5
Pb	NH_3+H_2	208		0.05	0.005	<1	<1	0.5

BEC and DL values of "0" are reported for Li and Ti because zero counts per second were measured for these elements in all 10 replicates of the blank UPW.

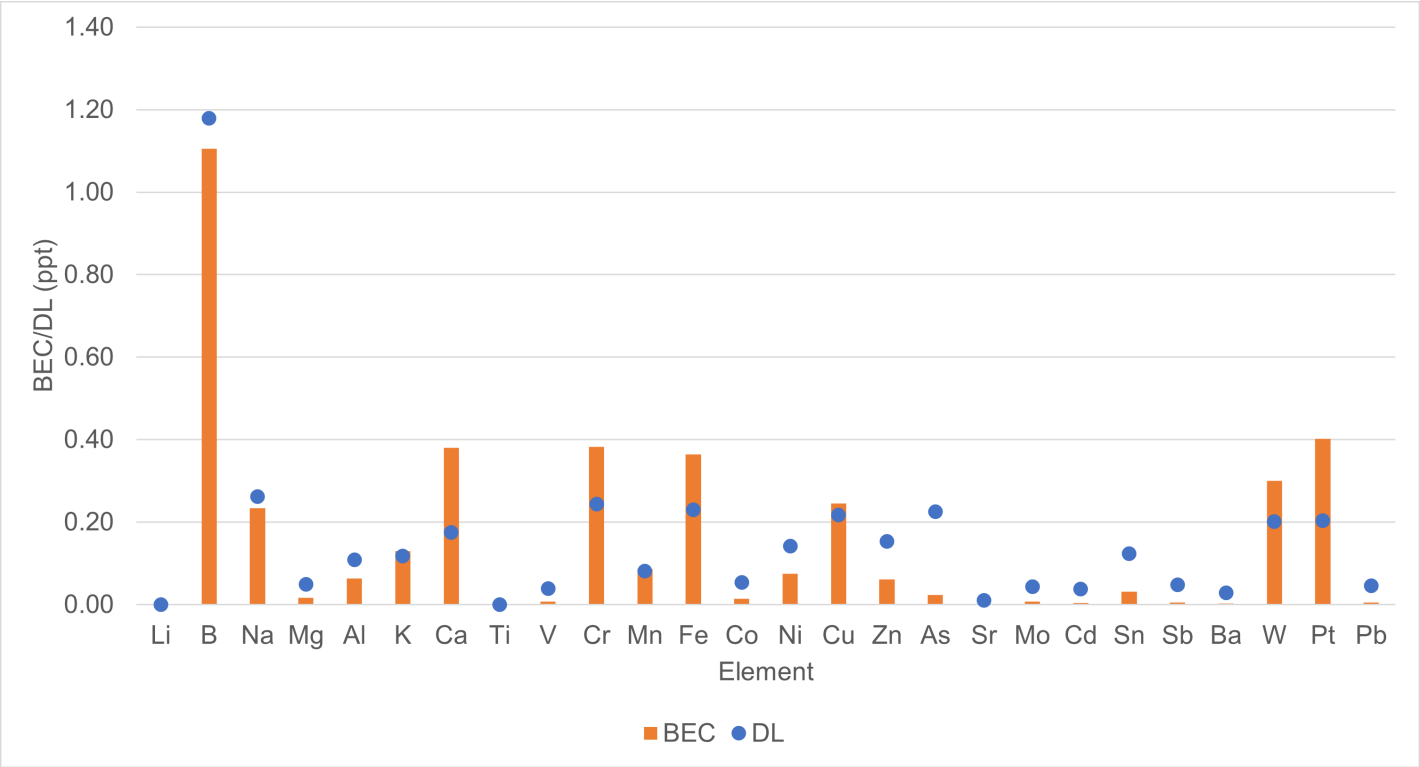

Figure 2. BECs and DLs for SEMI specified elements in UPW measured using the 8900 ICP-QQQ with hot plasma conditions.

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