Application Note

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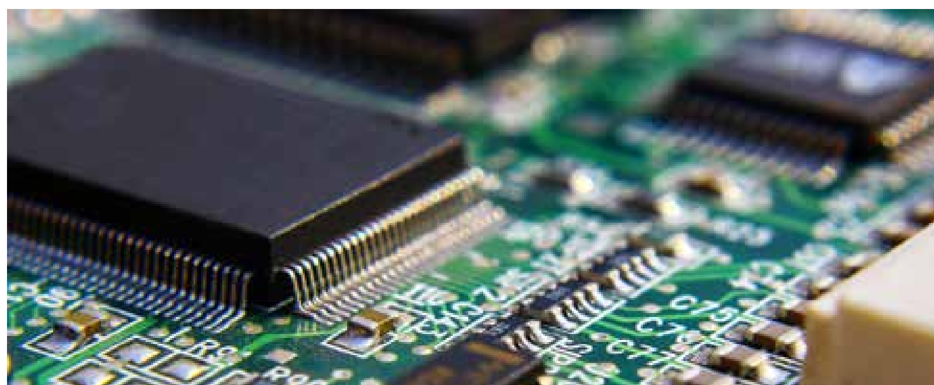
Direct Analysis of Trace Metal Impurities in High Purity Nitric Acid Using ICP-QQQ



Authors

Kazuo Yamanaka and Kazuhiro Sakai

Agilent Technologies, Tokyo, Japan

Introduction

The manufacturing yield of semiconductor devices has always been susceptible to contamination from trace metals. As the industry continues to progress towards devices with smaller features and a higher density of integration, susceptibility to contamination in microfabrication processing presents an increasing challenge. Controlling contamination at these small scales requires ever-higher purity of process chemicals and manufacturing conditions.

The semiconductor device fabrication industry uses well-established cleaning procedures to remove organic and metallic residues and impurities from the surface of silicon wafers. The purity of reagents used during manufacturing processes and the air quality in the fabrication plant are important considerations.

Nitric acid (HNO_3) plays an important role in the fabrication of semiconductor devices so needs to be of ultrahigh purity. A mix of nitric and hydrofluoric acid is used to etch single crystal silicon and polycrystalline silicon. HNO_3 is also combined with phosphoric acid and acetic acid for wet etching of aluminum. As a reagent, HNO_3 is used in the preparation of other semiconductor materials.

SEMI standard C35-0708 Tier-B protocol for HNO_3 (69.0–70.0 %) specifies contaminant levels of <1 µg/L (ppb) for several elements [1]. The concentration of industrial grade HNO_3 is usually 60–68%, depending on the method of production.

In this study, undiluted HNO_3 was analyzed directly by triple quadrupole ICP-MS (ICP-QQQ). This approach simplified sample preparation and avoided the potential introduction of contaminants during dilution.

Experimental

Samples and standards

Two samples of HNO_3 were used in this study:

- Sample 1: 68 % HNO_3 (high purity-grade)
- Sample 2: 61 % HNO_3 (electronic-grade - lower purity)

No further sample preparation was necessary as all samples were introduced directly into the ICP-QQQ.

Calibration and quantification were done using the method of standard additions (MSA). Standard solutions were prepared by spiking a multi-element standard solution (SPEX CertiPrep, NJ, US) into each HNO_3 sample to give spike levels of 5, 10, 20, 30 and 40 ppt. The density of the nitric acid solution varies with the concentration of the acid, which affects the sample transport, nebulization and droplet evaporation processes in the ICP-MS sample introduction. Therefore, for the most accurate analysis, the acid grade (concentration) used for the spiked MSA calibration solutions should be approximately matched to the acid concentration of the samples. ICP-MS MassHunter allows an MSA calibration to be converted to an external calibration to determine contaminant levels in other nitric acid samples with similar acid concentration. The solutions were prepared just before analysis. All preparation and analyses were performed in a Class 10,000 clean room.

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ instrument was used in this study. The instrument is fitted as standard with a PFA-100 nebulizer, Peltier-cooled quartz spray chamber, quartz torch, platinum-tipped sampling and skimmer cones, and s-lens. The nebulizer was operated in self-aspiration mode to minimize the potential for sample contamination from contact with the peristaltic pump tubing. If large numbers of undiluted HNO_3 samples are run 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.

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits (DLs) for each analyte. To achieve this goal, laboratories measuring ultratrace levels of contaminants can use a multitune method, where several tuning steps are applied sequentially during the measurement of each solution. This approach allows the tuning conditions to be optimized for the removal of different types of interferences, while maintaining sensitivity for each analyte. In this work, several reaction cell gases (He, H_2, O_2, and NH_3) and both hot and cool plasma conditions were used as appropriate for the large number of analytes being measured. Tuning conditions are shown in Table 1 and other acquisition parameters are shown in Table 2.

Table 1. ICP-QQQ operating conditions.

<table>
<tr><th></th><th>Cool-NH_3</th><th>No gas</th><th>H_2</th><th>He</th><th>O_2</th><th>O_2-soft</th></tr>
<tr><td>Acquisition mode</td><td colspan="6">MS/MS</td></tr>
<tr><td>RF power (W)</td><td>600</td><td colspan="5">1500</td></tr>
<tr><td>Sampling depth (mm)</td><td>18.0</td><td colspan="5">8.0</td></tr>
<tr><td>Nebulizer gas (L/min)</td><td colspan="6">0.70</td></tr>
<tr><td>Makeup gas (L/min)</td><td>0.78</td><td colspan="5">0.36</td></tr>
<tr><td>Extract 1 (V)</td><td>-150.0</td><td>4.2</td><td>4.7</td><td>4.2</td><td>4.5</td><td>3.5</td></tr>
<tr><td>Extract 2 (V)</td><td>-17.0</td><td colspan="4">-250.0</td><td>-120.0</td></tr>
<tr><td>Omega bias (V)</td><td>-70.0</td><td colspan="4">-140.0</td><td>-70.0</td></tr>
<tr><td>Omega lens (V)</td><td>2.0</td><td>10.0</td><td>8.0</td><td>10.0</td><td>10.5</td><td>4.0</td></tr>
<tr><td>Q1 entrance (V)</td><td>-15.0</td><td colspan="5">-50.0</td></tr>
<tr><td>He flow (mL/min)</td><td>1.0</td><td>-</td><td>-</td><td>5.0</td><td>-</td><td>-</td></tr>
<tr><td>H_2 flow (mL/min)</td><td>-</td><td>-</td><td>7.0</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>*NH_3 flow (mL/min)</td><td>2.0 (20%)**</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>O_2 flow (mL/min)</td><td>-</td><td>-</td><td>-</td><td>-</td><td colspan="2">0.45 (30%)**</td></tr>
<tr><td>Axial acceleration (V)</td><td>1.5</td><td colspan="3">0.0</td><td colspan="2">1.0</td></tr>
<tr><td>Energy discrimination (V)</td><td>-5.0</td><td>5.0</td><td>0.0</td><td>3.0</td><td colspan="2">-7.0</td></tr>
</table>

*10% NH_3 balanced with 90% He

** Values in parentheses are % of the maximum flow of the gas controller, as displayed in the tuning pane of ICP-MS MassHunter

Table 2. Acquisition parameters.

Parameter	Setting
Q2 peak pattern	1 point
Replicates	3 (spiked solution)
	10 (unspiked solution for DL measurement)
Sweeps/replicate	10
Integration time	2 s for all isotopes

Results and Discussion

DLs and BECs

In total, 49 elements were measured using the 8900 ICP-QQQ operating in multiple tune modes, switched automatically during a single visit to each sample vial. Data for each of the modes was combined automatically into a single report for each sample. DLs and Background Equivalent Concentrations (BECs) in undiluted 68% HNO_3 (Sample 1) are given in Table 3. The stability test results are discussed in the "long-term stability" section of the report.

Table 3. DLs and BECs in high purity 68% HNO_3.

Element	Tune	Q1	Q2	DL ng/L	BEC ng/L	30 ppt Recovery %	Stability test RSD %
Li	Cool-NH_3	7	7	0.061	0.042	93	3.1
Be	No gas	9	9	0.12	0.071	92	3.5
B	No gas	11	11	0.43	3.5	94	6.3
Na	Cool-NH_3	23	23	0.53	2.3	93	3.1
Mg	Cool-NH_3	24	24	0.085	0.049	93	2.0
Al	Cool-NH_3	27	27	0.10	0.16	93	3.6
P	O_2	31	47	8.1	83	95	—**
S	O_2	32	48	2.6	65	93	—**
K	Cool-NH_3	39	39	0.38	0.73	93	2.9
Ca	Cool-NH_3	40	40	0.54	0.38	93	1.2
Sc	O_2	45	61	0.007	0.013	93	0.5
Ti	O_2-soft	48	64	0.039	0.081	93	3.3
V	O_2-soft	51	67	0.041	0.17	93	1.5
Cr	Cool-NH_3	52	52	0.42	0.25	93	3.0
Mn	Cool-NH_3	55	55	0.084	0.014	93	2.5
Fe	Cool-NH_3	56	56	0.75	1.1	92	4.7
Co	Cool-NH_3	59	59	0.21	0.075	93	4.3
Ni	O_2-soft	60	60	0.067	0.38	93	2.0
Cu	Cool-NH_3	63	63	0.12	0.50	94	3.8
Zn	He	64	64	0.52	0.46	93	2.9
Ga	Cool-NH_3	71	71	0 cps	0 cps	92	2.5
Ge	H_2	74	74	0.060	0.10	93	1.4
As	O_2-soft	75	91	0.082	0.081	93	1.8
Se	H2	78	78	0.78	0.41	93	5.5
Rb	Cool-NH_3	85	85	0.089	0.030	93	3.0
Sr	He	88	88	0.014	0.012	93	0.8
Zr	O_2	90	106	0.22	1.0	93	0.4
Nb	He	93	93	0.012	0.014	93	0.8
Mo	He	98	98	0.088	0.10	93	1.0
Ru	He	101	101	0.032	0.034	93	1.2
Pd	No gas	105	105	0.066	0.14	92	1.0
Ag	No gas	107	107	0.029	0.025	93	0.9
Cd	No gas	114	114	0.058	0.046	92	1.4
In	No gas	115	115	0.004	0.004	93	0.6
Sn	No gas	118	118	0.099	0.35	93	0.9
Sb	H_2	121	121	0.056	0.028	93	1.6
Te	H_2	125	125	0.57	0.45	93	5.2
Cs	Cool-NH_3	133	133	0 cps	0 cps	93	2.4
Ba	H_2	138	138	0.014	0.010	93	0.4
Hf	No gas	178	178	0.014	0.005	93	0.9
Ta	He	181	181	0.052	0.065	93	0.5
W	No gas	182	182	0.030	0.022	93	0.7
Ir	No gas	193	193	0.016	0.011	93	0.9
Au	No gas	197	197	0.049	0.068	93	1.7
Tl	No gas	205	205	0.090	0.46*	93	0.6
Pb	No gas	208	208	0.060	0.21	93	0.7
Bi	No gas	209	209	0.018	0.025	93	0.4
Th	No gas	232	232	0.004	0.003	93	0.8
U	No gas	238	238	0.025	0.013	93	0.6

Table continues...

...Table continued

DLs were calculated as 3-sigma of 10 replicate measurements of a blank HNO_3 sample (cps refers counts per second).

**The BEC of Tl was higher than expected, most likely due to residual signal from the ICP-MS tuning solution.*

***P and S concentration in the mixed spike (30 ppt) was too low for reliable quantification above the blank (83 ppt and 65 ppt, respectively).*

Table 4 shows quantitative data for all SEMI specification elements [1] in high purity 68% HNO_3 and electronic-grade 61% HNO_3 determined by MSA. For the greatest accuracy, the two different concentration grades of nitric acid measured in this study were calibrated using separate MSA calibrations. However, if additional samples of similar grade (acid concentration) are measured, the MSA calibration can be easily and automatically converted to an external calibration plot. External calibration allows subsequent samples to be measured without requiring MSA spike additions into each additional sample.

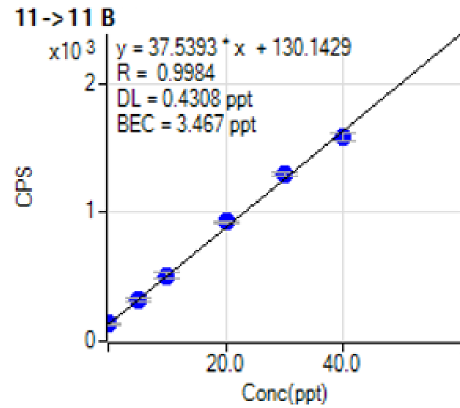
Good linearity was obtained for all SEMI target elements, as shown in the representative calibration curves for B, Na, Al, K, Ca, As, and Pb (Figure 1).

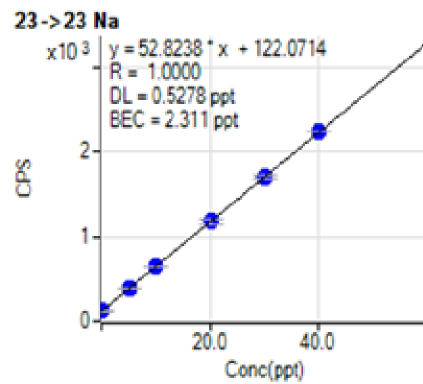
Normally, the concentration in each sample is obtained by multiplying the quantitative value by the dilution factor (usually about 10 times for nitric acid). However, in this study, the quantitative value equals the sample concentration in the original sample, as the acids were measured undiluted. The results given in Table 4 show that all 49 elements studied can be analyzed at significantly lower levels than the <1 ppb maximum limit specified for HNO_3 in SEMI standard C35-0708 Tier-B [1].

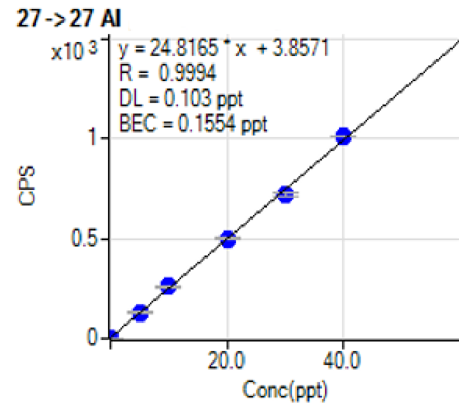
Table 4. Quantitative results for SEMI specification elements [1] in high purity 68% HNO_3 and electronic-grade 61% HNO_3.

Element	High-purity grade 68% HNO_3, ng/L	Electronic grade 61% HNO_3, ng /L	SEMI C35-0708 Tier-B max limit, ng/L
Li	<0.061	0.19	<1000
B	3.5	270	<1000
Na	2.3	130	<1000
Mg	<0.085	11	<1000
Al	0.16	93	<1000
K	0.73	6.5	<1000
Ca	<0.54	50	<1000
Ti	0.081	1.1	<1000
V	0.17	0.24	<1000
Cr	<0.42	70	<1000
Mn	<0.084	3.4	<1000
Fe	1.1	270	<1000
Ni	0.38	28	<1000
Cu	0.50	0.99	<1000
Zn	<0.52	3.8	<1000
As	<0.082	0.25	<1000
Cd	<0.058	0.80	<1000
Sn	0.35	13	<1000
Sb	<0.056	0.11	<1000
Ba	<0.014	0.43	<1000
Pb	0.21	0.31	<1000

Measured values shown as "<" indicate that the measured concentration was below the detection limit.







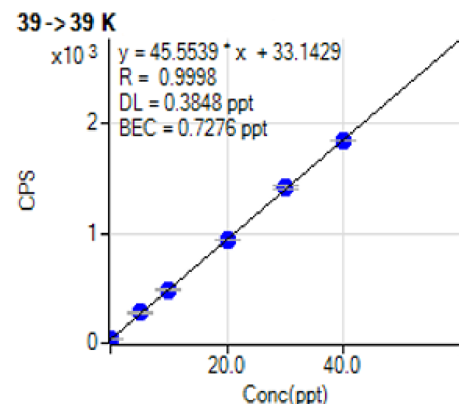
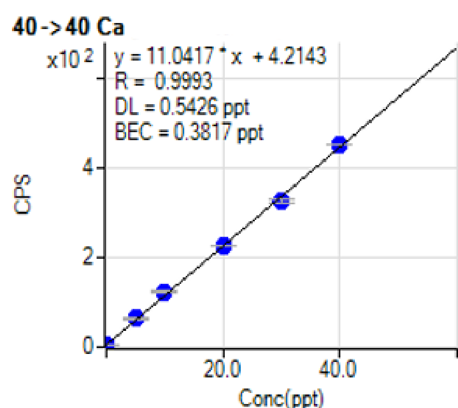
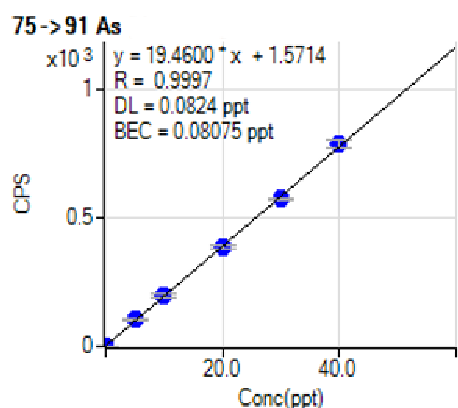


Figure 1. Calibration curves for several SEMI specification elements in high purity 68% HNO_3





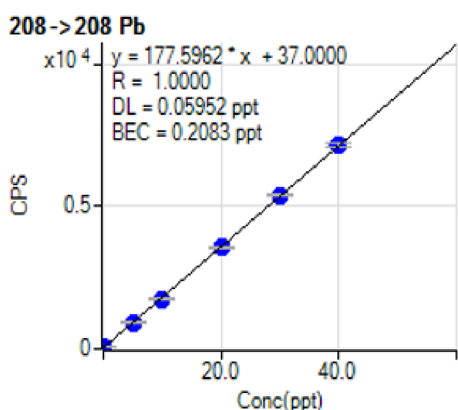


Figure 1. (continued) Calibration curves for several SEMI specification elements in high purity 68% HNO_3.

Long-term stability

Long-term stability was evaluated by measuring a 68% HNO_3 sample spiked at 30 ppt for all elements. Calibration curves were generated at the beginning of the sequence. The spiked samples were then run as unknown samples for a total analysis period of 6.5 hours. The RSDs of the 21 analysis results are shown in Table 3 (stability test RSD (%)). Good stability was maintained throughout the run, with RSDs between 0.4 and 5.5 %. S and P gave less reliable long-term results due to the low concentration of the spike (30 ppt) measured above the relatively high concentration (83 ppt for P; 65 ppt for S) in the unspiked sample.

Conclusions

The Agilent 8900 ICP-QQQ operating in MS/MS mode provides the sensitivity, low backgrounds, and unmatched control of interferences required for the analysis of ultratrace elements in high purity nitric acid.

Forty-nine elements were measured at sub-ppt to ppt levels in undiluted high purity 68% HNO_3. Calibrations were linear for all elements between 0–40 ppt. SEMI-specified elements were quantified at the single-figure ppt or sub-ppt level in high purity 68% HNO_3. The reproducibility results for 30 ppt spikes in high purity undiluted 68% HNO_3 were between 0.4–5.5 % RSD for all elements except P and S, in a sequence lasting 6.5 hours.

The results demonstrate the suitability of the Agilent 8900 Semiconductor configuration ICP-QQQ for the routine analysis of the highest-purity semiconductor-grade reagents and process chemicals.

References

1. SEMI C35-0708, Specifications and guidelines for nitric acid (2008).

More Information

For more information on Agilent ICP-MS products and services, visit our website at www.agilent.com/chem/icpms

When analyzing 61–68 % HNO_3 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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