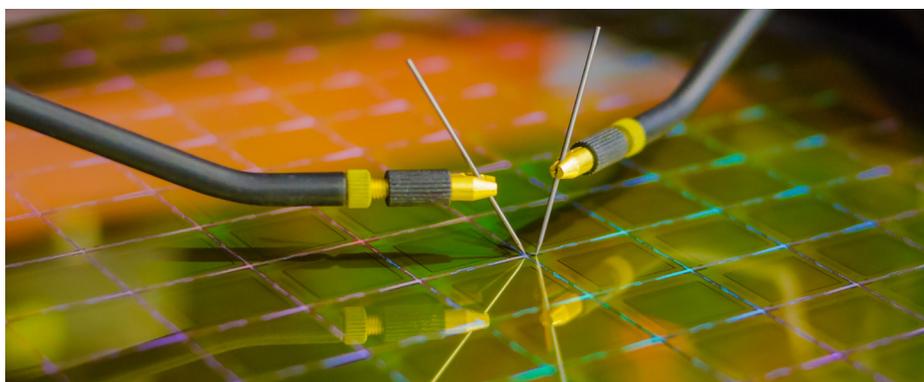


Analysis of Metallic Impurities in Specialty Semiconductor Gases Using Gas Exchange Device (GED)-ICP-MS

Measuring total metals and nanoparticles in HF and Cl₂ gases using ICP-QQQ with GED and Metal Standard Aerosol Generation



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Introduction

Semiconductor devices are so widely used in everyday electronic objects that they have become an indispensable part of modern life. Technologies associated with the design and manufacture of integrated circuits (ICs) continue to evolve to meet industry demands for faster and smaller chips with higher integration densities and lower energy consumption. As the architecture of ICs develops, the structure is getting more complicated, line widths are narrowing, and the number of production steps is increasing. The quality control of the chemicals used in the semiconductor industry needs to keep pace with the developments in chip design.

Various high purity, specialty gases are used in IC manufacturing. For example, hydrogen fluoride (HF) is used to etch and clean silicon wafers and chlorine (Cl₂) is used to plasma etch aluminum and other metal layers. As impurities present in the gases may impact the yield or performance of the final device, analysis of these types of gases is important.

A highly sensitive analytical technique such as ICP-MS is commonly used to determine ultratrace-levels of metallic contamination—dissolved elements and insoluble nanoparticles (NPs)—in chemicals used throughout the manufacturing of ICs (7). Typically, metallic impurities in gases include single element particles or compounds (particulate or gaseous) that contain multiple elements. However, gases are difficult to analyze directly by ICP-MS as even a small amount of these gases will extinguish the argon (Ar) plasma of the ICP-MS. Also, there are no metallic gas standards available for the quantitation of particles.

The IAS Gas Exchange Device (GED) introduction system for ICP-MS is a proven technique that has been used to analyze airborne particulate matter (2–4). The principles of the technique are outlined in Figure 1. A sample gas that contains metallic particles is introduced inside the membrane while an Ar sweep gas flows on the outside of the membrane. Because the Ar sweep gas flow is much higher than the sample gas flow, the sample gas is almost completely exchanged (>99.99%) by Ar gas. Particles cannot pass through the membrane, so they exit the GED in the central Ar gas stream, which is then introduced to the plasma of the ICP-MS for analysis. When the particles are analyzed, the speed of the sample gas flow within the sample gas line tubing is important. It must be optimized to minimize particle loss due to Brownian motion for smaller particles and gravitational forces on larger particles (5).

For the analysis of particles, single nanoparticle (sp) analysis mode is used. Using a shorter dwell time, spICP-MS can easily distinguish the signals from small particles above the background noise (6, 7). However, as gases are exchanged with Ar gas by the GED membrane, the GED cannot be used for the analysis of gaseous impurities. The direct introduction of gas samples to the ICP-MS is possible using a GED without a membrane and spectrum data analysis mode set by the software. The GED software can do both analyses (spectrum and single nanoparticle) automatically.

For the analysis of important but corrosive gases such as HCl, HF, Cl₂, and NH₃, a new GED has been developed that uses a membrane enclosed in an electropolished stainless steel cell. The cell is used in two IAS GED models: the GED_SEMI, which has six gas inlet lines, and the GED_LAB, which has one gas inlet line.

An IAS Metal Standard Aerosol Generation (MSAG) unit is also needed for the quantitative analysis of gases by GED-ICP-MS (Figure 2). The MSAG introduces a few µL/min of an aqueous elemental standard solution to a specially designed nebulizer operating with a gas flow rate of 0.3 L/min of Ar. The system introduces all the standard solution to the plasma of the ICP-MS. Therefore, an absolute amount of standard solution introduced to the plasma can be calculated mathematically by the MSAG software. The sensitivity factor in ag/count (10⁻¹⁸ g/count) can then be calculated from the intensity of the ICP-MS signal. When the signal is measured by the ICP-MS in transient time resolved analysis (TRA) mode, the weight of one particle can be obtained from the sensitivity factor, which corresponds to the diameter of the particle detected. The concentration of particles can be calculated from the total amount (weight) of particles detected and the total sample gas amount introduced to the plasma during the analysis. The data, which is processed by the MSAG software, is automatically sent to the GED software for reporting of the final results.

In this study, the GED_LAB was integrated with the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) for the analysis of HF and Cl₂ gases. Using the Agilent Software Developer's Kit (SDK) for ICP-MS MassHunter, IAS developed software to fully control the GED-MSAG-ICP-MS workflow from the GED software.

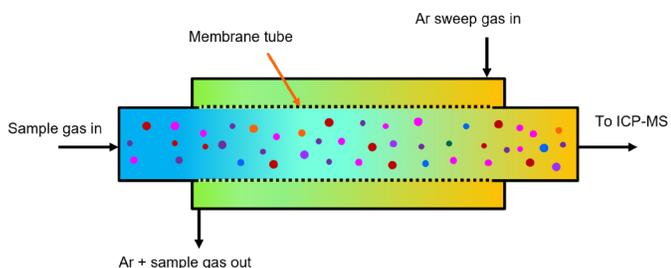


Figure 1. Principles of the IAS Gas Exchange Device. Reproduced with permission from IAS.

Experimental

Reagents and samples

For calibration of the ICP-MS, a 10 ppb stock standard solution was prepared in 0.5% HNO₃ from a 10 ppm multi-element standard solution (XSTC-622B, SPEX CertiPrep, NJ, USA). A 0.5% HNO₃ acid blank and standard diluent was prepared using TAMAPURE AA-100 HNO₃ (Tama Chemicals Co., Ltd., Kanagawa, Japan). De-ionized water (DIW) was produced using the Puric ω (Organo Corp., Tokyo, Japan). All chemicals were prepared in an ISO Class 5 cleanroom. The sample gases, gas pressure regulators, and particle filter were bought from a gas company in Japan.

Instrumentation

A schematic of the GED-MSAG-ICP-MS technique is shown in Figure 2. The system was configured with a filter inserted in the sample gas line. To check if particles originated from the sample gases, the analysis was performed using the GED membrane with and without the filter. To analyze gaseous impurities in the sample gases, a small amount of the sample gas was introduced directly to the plasma of the ICP-MS via the diluent Ar gas, bypassing the membrane.

For calibration and quantitation, the MSAG introduced a fixed amount of solution at 3 μL/min from two syringes. This method avoided matrix effects caused by the addition of an aqueous standard solution into a dry plasma. An acid blank and a multi-element standard solution were introduced from each syringe of the MSAG. Calibration curves were prepared by changing the ratio of the acid blank and the standard solution.

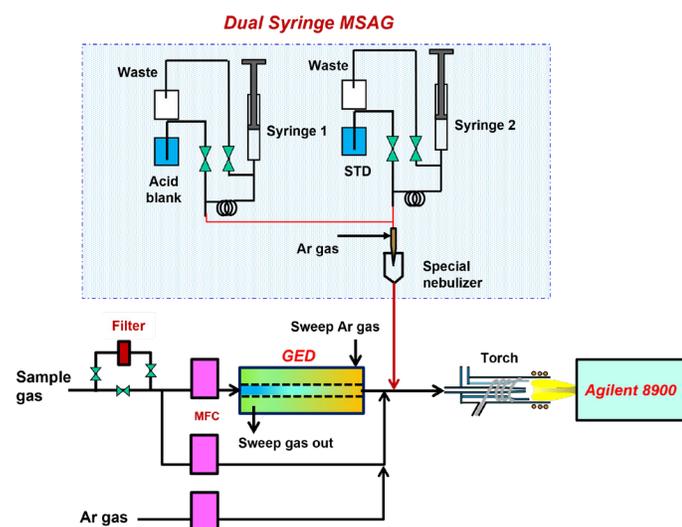


Figure 2. Schematic diagram of the GED-MSAG system coupled to the Agilent 8900 ICP-MS. Reproduced with permission from IAS.

Operating conditions of the GED used for the analysis of semiconductor-grade HF and Cl₂ gases are given in Table 1.

Table 1. IAS GED_LAB operating parameters.

Parameter	Value	
	HF	Cl ₂
Sample gas flow for particle analysis (mL/min)	1,000	400
Sweep Ar gas flow (mL/min)	6,000	4,000
Sweep gas outlet pressure (kPa)	9.8	9.8
MSAG nebulizer Ar gas flow (mL/min)	300	300
MSAG 10 ppb standard solution flow (μL/min)	1	1
Ar makeup gas flow (mL/min)	450	300
Sample gas flow for direct analysis (mL/min)	5	1
Ar dilution gas flow for direct analysis (mL/min)	1,130	1,230

The 8900 Semiconductor configuration ICP-MS was fitted with a standard configuration, HF-tolerant PFA inert torch with a 2.5 mm Pt 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 m-lens was used to obtain lower detection limits for alkali metals.

The GED software was used to set up the ICP-MS method 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 NH₃ and He cell gases), and oxygen reaction mode were used to remove interferences using a combination of on-mass and mass-shift measurements. 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. The same plasma conditions were used for all gas modes. Instrument acquisition and operating parameters are given in Table 2. The basic tuning of the 8900 ICP-MS was performed by introducing Ar gas with a 1 μL/min of a 10 ppb stock standard solution from the MSAG, followed by optimization with each sample gas. A flow rate of 2 μL/min was used for the 0.5% HNO₃ blank solution.

To minimize the analysis time, the calibration curves were created by the method of standard addition (MSA) using spectrum acquisition mode for all elements. When the particle analysis was performed, Single Nanoparticle acquisition mode with a 1 ms dwell time and the same tuning parameters were used.

Table 2. Agilent 8900 ICP-QQQ operating parameters.

Parameter	Value		
	No gas	NH ₃ / He	O ₂
Scan Mode	MS/MS		
Sampling Depth (mm)	15		
RF Power (W)	1,200		
Cell Gas Flow	-	NH ₃ 35% He 1 mL/min	25%

Results and discussion

Hydrogen fluoride (HF)

Particle analysis

Figure 3 shows the particle analysis results for HF obtained using the single nanoparticle acquisition mode with a 1 ms dwell time. The horizontal axis represents data acquisition time, and the vertical axis shows ICP-MS signal intensity in counts per 1 ms. The ion intensity is proportional to the mass of the target element in the original particle, allowing for the determination of the particle size, assuming spherical particles.

The data in Figure 3 shows the presence of many different-sized particles of elements such as Fe, Ni, Cr, Mn, Na, K, Ca, Sn, and W in unfiltered HF, and significantly fewer Fe particles in the filtered HF gas. These results clearly show that most particles passed through the GED and were detected by the ICP-MS. Relatively few small-sized particles containing Cu, Zn, Al, Sb, and Ti were detected above the background signal.

The short dwell time (1 ms) of single nanoparticle acquisition mode ensures low background counts on each data point. The single nanoparticle acquisition mode easily determined small sized particles for many different elements, as shown in Figure 3.

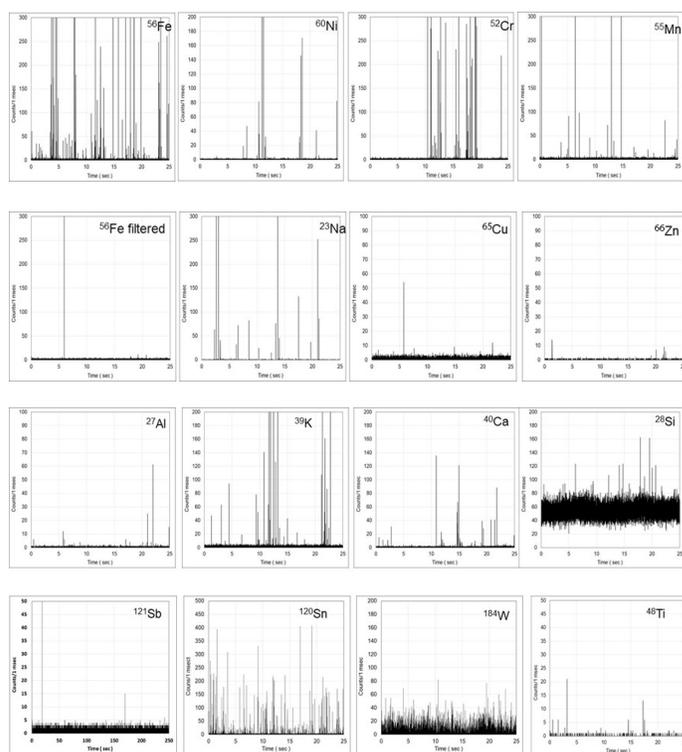


Figure 3. Transient signal of elements in HF gas using GED-ICP-MS in spICP-MS mode.

Si, Sb, and W showed a high continuous background due to the presence of many small-sized particles or gaseous impurities.

Analysis of gaseous impurities

To investigate gaseous impurities, HF gas was introduced directly to the ICP-MS at a 5 mL/min flow rate together with Ar dilution gas. Figure 4 shows the intensity trend of some elements in HF from a gas cylinder that was left undisturbed overnight. B, Ge, Sr, Sn, and Sb were analyzed by ICP-MS after opening the gas cylinder valve. Initially the signals for Sb, Sn, Ge, and B increased before falling rapidly within 5 minutes and then more gradually for the next 5 minutes. These results show that it is best practice to wait for an equilibrium of gas and liquid phases in the HF gas cylinder before analysis. Spiky signals of Sb and Sn were detected after 11 minutes, which might be caused by boiling of HF solution in the HF gas cylinder.

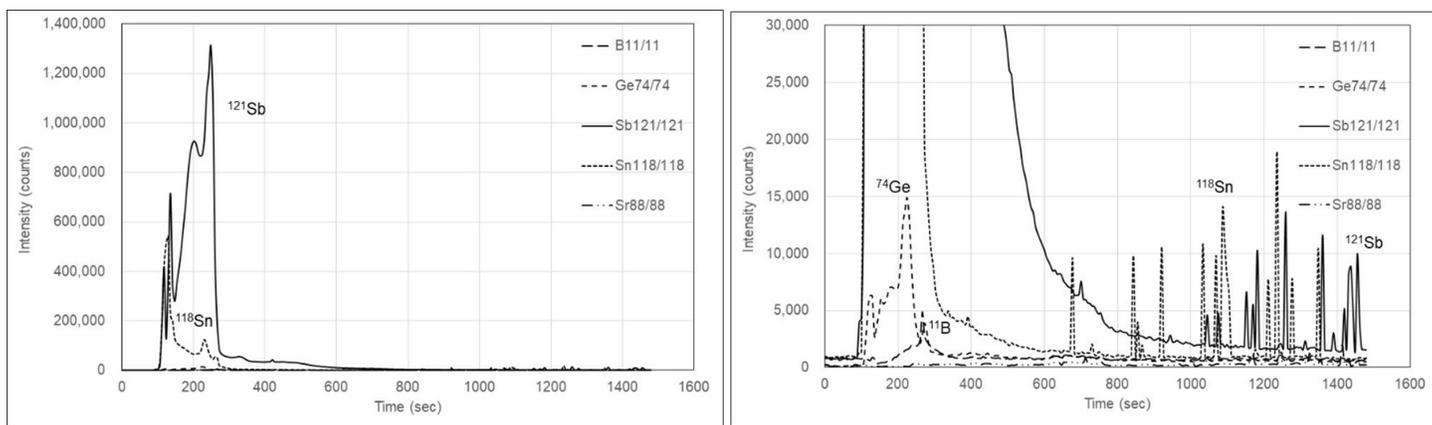


Figure 4. Trend of elements in HF gas after opening the valve (same data shown using different intensity scales on the Y-axis).

For the direct analysis of HF using spectrum acquisition mode, a 1 s integration time per mass was used. The sensitivity factors (calculated by the software) of the Ar gas blank and the HF gas sample are given in Table 3. Some elements such as B, P, Cu, Ge, and W showed higher signals in the HF gas than the Ar gas blank, likely due to volatile fluoride compounds. The sensitivity factors of HF gas were slightly higher than for Ar gas for most elements, due to the HF matrix. Since B and P background counts were higher than other elements, a higher concentration of these elements in the MSAG standard solution would be needed to improve the accuracy of the sensitivity factors.

Gaseous metallic and particulate impurities in HF

A summary of the gaseous metallic and particulate impurities in HF gas is given in Table 3. As previously stated, the direct gas analysis uses spectrum acquisition mode with a 1 s integration time, whereas the single nanoparticle acquisition mode uses TRA mode with a 25 s measurement time. All data was automatically calculated by the GED software using the sensitivity factor and the weight of HF gas introduced (based on the respective flow rates and integration times of the two methods).

Particles of Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Zn, Ge, and Ba were detected using the GED-spICP-MS method whereas these elements were not detected using the direct gas analysis method. The GED-spICP-MS concentration data was reported in ng/kg. These units are 1,000 times lower than the data reported using spectrum mode ($\mu\text{g}/\text{kg}$) because GED-spICP-MS uses a much higher gas flow rate for the sample gas than the direct gas method.

Table 3. Summary of HF gas analysis results showing gaseous impurity data obtained by direct gas ICP-MS analysis in spectrum acquisition mode and particulates obtained by GED-ICP-MS in single particle analysis mode.

Analyte	Q1 Mass	Q3 Mass	Gaseous Impurities						Particulates	
			Integration Time (s)	Ar Gas		HF Gas		Blank Corrected Conc (µg/kg)	HF Gas	
				Sensitivity Factor (ag/count)	Conc (µg/kg)	Sensitivity Factor (ag/count)	Conc (µg/kg)		Integration Time (s)	Conc (ng/kg)
Li	7	7	1	19	< 0.002	15	0.003	N.D.	25	N.D.
B	11	11	1	14	2	88	99	97	25	N.D.
Na	23	23	1	10	0.09	11	2	1	25	0.02
Mg	24	24	1	16	< 0.003	16	< 0.002	N.D.	25	0.006
Al	27	27	1	29	< 0.01	31	< 0.01	N.D.	25	0.008
P	31	47	1	93	0.6	12	124	123	25	N.D.
K	39	39	1	7	0.1	7	0.1	N.D.	25	0.03
Ca	40	40	1	24	< 0.06	26	< 0.06	N.D.	25	0.03
Ti	48	64	1	28	< 0.005	29	0.1	0.1	25	0.007
V	51	51	1	23	< 0.003	24	0.008	0.005	25	N.D.
Cr	52	52	1	23	< 0.007	27	0.023	0.02	25	0.1
Mn	55	55	1	14	0.012	16	0.007	N.D.	25	0.1
Fe	56	56	1	17	0.01	20	0.03	0.02	25	0.8
Co	59	59	1	20	< 0.004	23	< 0.004	N.D.	25	0.002
Ni	60	60	1	92	<0.07	106	<0.07	N.D.	25	0.1
Cu	65	65	1	12	0.006	15	0.3	0.3	25	0.02
Zn	66	66	1	137	<0.08	177	< 0.04	N.D.	25	0.009
Ga	69	69	1	18	< 0.003	23	0.009	0.006	25	N.D.
Ge	74	90	1	38	0.02	40	0.2	0.2	25	0.03
As	75	91	1	167	0.2	172	418	418	25	N.D.
Se	80	96	1	2,012	< 0.3	2,198	0.8	0.5	25	N.D.
Sr	88	88	1	10	< 0.003	11	< 0.003	N.D.	25	N.D.
Zr	90	90	1	17	< 0.002	21	< 0.002	N.D.	25	N.D.
Mo	98	98	1	48	< 0.01	57	0.05	0.04	25	N.D.
Ag	107	107	1	22	< 0.003	26	< 0.007	N.D.	25	N.D.
Cd	111	111	1	26	< 0.002	29	0.02	0.02	25	N.D.
Sn	118	118	1	32	< 0.009	39	0.03	0.02	25	1
Sb	121	121	1	37	0.02	43	0.05	0.03	25	0.5
Ba	138	138	1	11	< 0.002	11	< 0.001	N.D.	25	0.002
W	184	184	1	31	< 0.008	29	0.04	0.03	25	0.09
Pb	208	208	1	17	< 0.004	16	< 0.003	N.D.	25	N.D.

Chlorine (Cl₂)

Figure 5 shows the particle analysis results for Cl₂ gas acquired using GED-ICP-MS in spICP-MS mode with and without a filter. With no filter fitted, a high number of Ca, Cr, Mn, Fe, Ni, and Cu particles were detected, while P, Ge, As, Sn and Sb showed a continuous background likely caused by volatile chloride compounds.

Low counts were observed for Ba, W, and Bi. However, the frequency of one count-signals without the filter was higher than with the filter, which may be due to small particles, as Ba, W, and Bi do not form volatile chloride compounds.

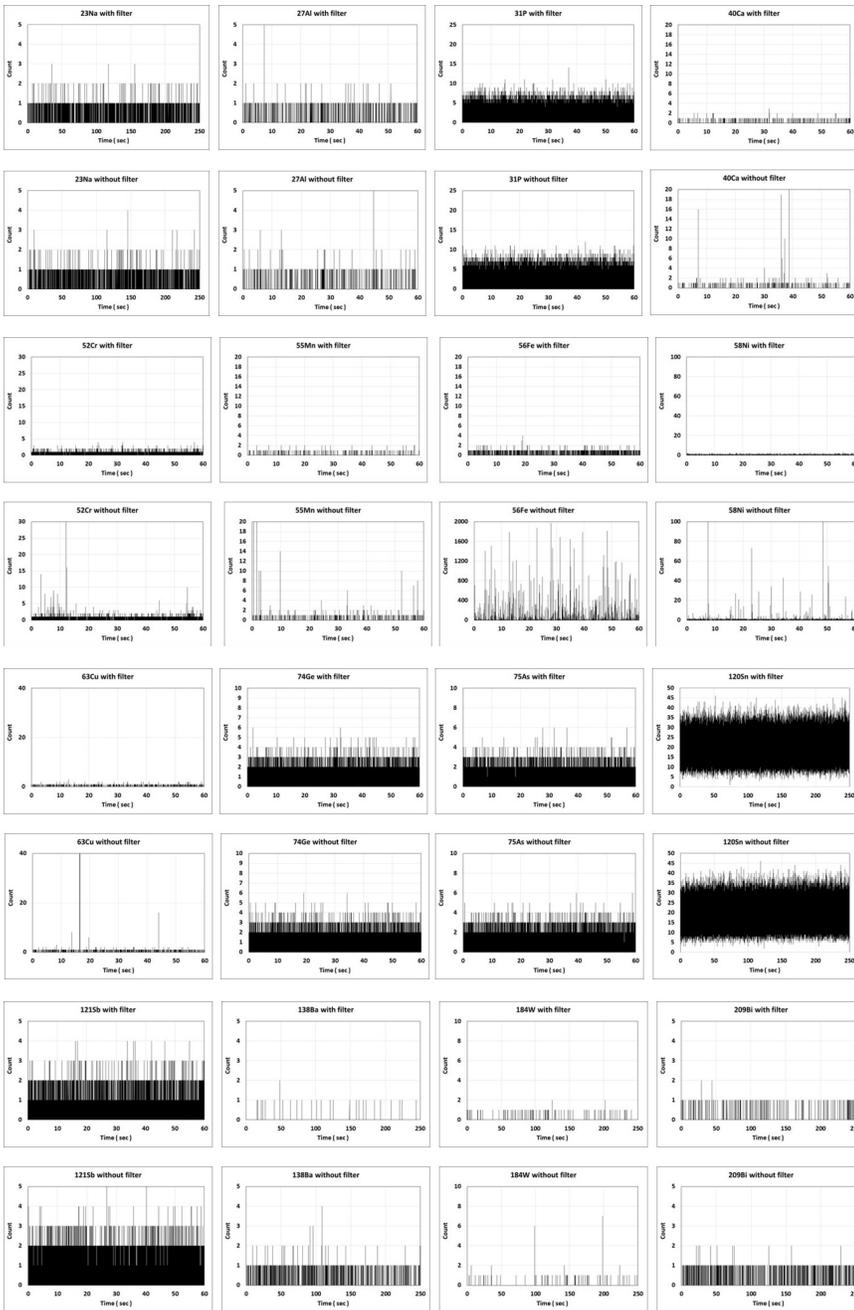


Figure 5. Transient signal of elements in Cl₂ gas using GED-ICP-MS in spICP-MS mode with and without a filter.

A summary of gaseous metallic and particulate impurities in Cl₂ gas is given in Table 4. The direct gas analysis showed relatively high concentrations of P, Fe, Cu, Ge, As, Sn, and Sb, which form volatile chloride compounds. The GED-spICP-MS analysis detected some particulate impurities at much lower concentration levels.

Table 4. Summary of Cl₂ gas analysis results showing gaseous impurity data obtained by direct gas ICP-MS analysis in spectrum acquisition mode and particulates obtained by GED-ICP-MS in single particle analysis mode.

Analyte	Q1 Mass	Q3 Mass	Gaseous Impurities						Particles	
			Integration Time (s)	Ar Gas		Cl ₂ Gas		Blank Corrected Conc (µg/kg)	Cl ₂ gas	
				Sensitivity Factor (ag/count)	Conc (µg/kg)	Sensitivity Factor (ag/count)	Conc (µg/kg)		Integration Time (s)	Conc (ng/kg)
Li	7	7	0.45	60	0.000	47	0.002	0.003	250	N.D.
Na	23	23	0.45	22	< 0.003	18	0.01	0.009	250	0.001
Mg	24	24	0.45	37	0.000	36	0.000	N.D.	250	N.D.
Al	27	27	0.45	32	0.008	44	0.01	0.002	60	N.D.
P	31	47	0.45	363	161	431	941	780	60	N.D.
K	39	39	0.45	18	0.02	24	0.02	N.D.	60	N.D.
Ca	40	40	0.45	22	0.007	26	0.003	N.D.	60	0.001
Ti	48	64	0.45	28	< 0.002	31	0.000	N.D.	60	N.D.
V	51	51	0.45	25	0.000	41	0.1	0.1	60	N.D.
Cr	52	52	0.45	20	0.5	36	1	0.8	60	0.002
Mn	55	55	0.45	12	< 0.002	26	< 0.001	N.D.	60	0.004
Fe	56	56	0.45	15	0.02	33	21	21	60	2.3
Ni	58	58	0.45	34	0.05	71	0.2	0.2	60	0.036
Co	59	59	0.45	16	< 0.001	18	0.000	N.D.	60	N.D.
Cu	63	63	0.45	36	0.02	86	3	3	60	0.006
Zn	66	66	0.45	92	0.000	310	0.3	0.3	60	N.D.
Ga	69	69	0.45	17	0.000	35	0.03	0.03	60	N.D.
Ge	74	74	0.45	21	0.02	70	3	3	60	N.D.
As	75	91	0.45	271	< 0.1	791	43	43	60	N.D.
Sr	88	88	0.45	11	< 0.001	12	0.000	N.D.	60	N.D.
Zr	90	106	0.45	20	< 0.005	22	0.000	N.D.	60	N.D.
Mo	98	98	0.45	55	< 0.007	82	< 0.05	N.D.	60	N.D.
Ag	107	107	0.45	23	< 0.003	26	0.000	N.D.	60	N.D.
Cd	111	111	0.45	32	< 0.004	35	0.000	N.D.	250	N.D.
Sn	120	120	0.45	35	1	38	60	59	250	0.21
Sb	121	121	0.45	37	0.07	43	2	2	60	0.24
Ba	138	138	0.45	13	< 0.001	14	< 0.001	N.D.	250	0.002
W	184	184	0.45	32	< 0.004	29	0.000	N.D.	250	N.D.
Pb	208	208	0.45	18	< 0.002	17	0.000	N.D.	60	N.D.

Conclusion

GED-MSAG-ICP-MS was used for the analysis of gaseous metallic impurities and particulates in gases used in the semiconductor industry. Assessing total metal impurity levels in specialty gases is an increasingly important application as ICs get smaller, faster, and more energy-efficient.

To handle corrosive gases such as HF and Cl₂, the GED was equipped with a membrane enclosed in an electropolished stainless steel cell. The dual syringe MSAG was used to automatically calibrate the Agilent 8900 ICP-QQQ using MSA by introducing controlled concentrations of an acid blank and a multi-element standard solution.

The high sensitivity, low backgrounds, and effective control of interferences using MS/MS allowed the 8900 ICP-QQQ to monitor both dissolved gaseous contaminant elements and nanoparticles in the gases at low concentrations.

Operating the 8900 ICP-QQQ in single particle (sp)-ICP-MS mode using a dwell time of 1 ms, the GED-MSAG-ICP-MS technique detected various metallic particles in HF and Cl₂ gases. For the analysis of gaseous metallic impurities that were lost in the GED membrane, HF and Cl₂ were introduced directly (no GED) to the plasma of the ICP-QQQ via an Ar diluent gas. The data was acquired in spectrum acquisition mode and the results showed the range of gaseous metallic impurities that were detected in the gases.

The GED-MSAG-ICP-MS technique can also be used to test other specialty gases of interest to the semiconductor industry, including NH₃, CO₂, HCl, NF₃, SiH₂Cl₂, and SF₆.

Warning Chemical Hazard

This method does not address safety issues associated with its use. It is the responsibility of the analyst to use all appropriate personal protective equipment and follow all appropriate safety procedures.

www.agilent.com/chem/8900icp-qqq

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References

1. Measuring Inorganic Impurities in Semiconductor Manufacturing, Agilent publication, [5991-9495EN](#)
2. Kohei Nishiguchi et al., Real-time multielement monitoring of airborne particulate matter using ICP-MS instrument equipped with gas converter apparatus, *J. Anal. At. Spectrom.*, **2008**, 23, 1125–1129
3. Robert Kovacs et al., Development of direct atmospheric sampling for laser ablation-inductively coupled plasma-mass spectrometry, *J. Anal. At. Spectrom.*, **2010**, 25, 142–147
4. Yoshinari Suzuki et al., Real-time monitoring and determination of Pb in a single airborne nanoparticle, *J. Anal. At. Spectrom.*, **2010**, 25, 947–949
5. S.-L. von der Weiden et al., Particle loss calculator – a new software tool for the assessment of the performance of aerosol inlet systems, *Atoms. Meas. Tech. Discuss.*, **2009**, 1099–1141
6. Yoshinori Shimamura, Donna Hsu, and Michiko Yamanaka, Multielement Nanoparticle Analysis of Semiconductor Process Chemicals Using spICP-QQQ, Agilent publication, [5994-0987EN](#)
7. Donna Hsu, Yoshinori Shimamura, Brian Liao, Michiko Yamanaka, Chun-Hua Chen, Chiu-Hun Su, and Ching Heng Hsu, Analysis of Nanoparticles in Organic Reagents by Agilent 8900 ICP-QQQ in spICP-MS Mode, Agilent publication, [5994-1306EN](#)

