APPLICATION NOTE

ICP - Mass Spectrometry

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Direct Analysis of Metallic Impurities in Hydrochloric Gas Using Gas Exchange Device (GED) ICP-MS

Introduction

In today's fast-paced world, semiconductors have become an indispensable device. Demands for faster and smaller chips with higher integration and lower energy consumption are increasing. Consequently, device structures are becoming more complicated, resulting in an increase in the number of production steps: deposition, lithography, etching, ashing, planarization, cleaning and drying. With narrower line widths, metal contamination needs to be tightly controlled in manufacturing processes to the low ppt-ppq range. Potential sources of metallic contamination in semiconductor manufacturing processes are ubiquitous, from the Si wafer itself, gases and chemicals used in processing, right through to the facility and equipment. Therefore, it is essential to have instrumentation which is capable of accurately measuring metal contamination at these ultra-trace levels.

For this reason, inductively coupled plasma mass spectrometry (ICP-MS) is the most common analytical tool for detecting metal impurities in the semiconductor field given its outstanding detection capabilities. Analytical methods currently used for the control of metallic contamination in the semiconductor manufacturing industry are listed below:

1. *Analysis of a dummy Si wafer after vapor phase decomposition (VPD):* Metallic impurities in films can be deposited onto a silicon (Si) wafer during Si wafer surface etching, ashing, cleaning or drying and imbedded in the wafer during the process of implantation. For these contaminants, the Si wafer itself can be analyzed by VPD-ICP-MS.[1] Although this technique is beneficial in that it can evaluate contamination from the overall processes, the challenge is that it does not allow for the identification of the source of the contamination. This technique has been used as an inline tool in semiconductor fabrication (FAB), and has been integrated with AMHS (Automatic Material Handling System) and SECS (SEMI Equipment Communication Standards)/HSMS (High-Speed SECS Message Services)/GEM300 (Generic Model for Communication and Control of Manufacturing Equipment) for 24/7 operation.

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2. *Analysis of chemicals used for cleaning, etching, drying and lithography:* These chemicals can be analyzed directly or after dilution by ICP-MS. This step evaluates metallic contamination in semiconductor chemicals from lorries, storage tanks and canisters. Inline systems for this application also allow for 24/7 operation.

3. *Analysis of gases used for deposition, etching, ashing and purging:* Gases used in these processes can be a source of both total and particulate elemental contamination. These gases are often considered difficult to analyze directly by ICP-MS because the argon plasma of ICP-MS systems only allows a small volume of gas to be introduced. Furthermore, there are only a few gases which have been characterized for metal content to date, making calibration for this application particularly challenging. For these reasons, a gas bubbling technique using an impinger followed by the ICP-MS analysis has been most commonly used to date. This approach works on the principle that when a gas is introduced into a solution in an impinger, metallic impurities will be deposited into the solution. It has been found, however, that when an air sample with particles was evaluated using this method, only small particles, e.g. 5 nm, were sufficiently retained by the solution (>80%) while larger particles (>30 nm) were insufficiently retained at around 10% retention.[2] The root cause was determined to be that when a gas is bubbled into the solution, the gas only has partial contact with the solution, resulting in the observed low retention. When highly soluble gases, such as hydrochloric acid (HCl) and ammonia (NH_3), are introduced into the impinger, it may cause backflow of the trapping solution. In order to avoid this issue, a small amount of inert gas, such as N_2, is usually added. However, in this case, the outgassed N_2 gas bubbles are often accompanied by particles, thereby lowering their concentration in the trapping solution. After bubbling, the solution is manually transferred to the ICP-MS for analysis. This procedure, however, is time consuming and causes a higher risk of contamination. Therefore, there is strong demand for a simpler and faster analytical technique.

Gas exchange device (GED) is a technology that can analyze metal particles in gases and has historically been used for the analysis of particles in the atmosphere.[3,4,5] With this technique, a sample gas is introduced to an inner side of the membrane tube and an argon (Ar) sweep gas is introduced to an outer side of the membrane tube, as shown in Figure 1. Since the partial pressure of the sample gas inside the membrane tube is higher than that on the outside, the sample gas diffuses into the outside of the membrane tube. On the other hand, the partial pressure of Ar gas outside the membrane tube is higher than on the inside and the Ar gas diffuses into the inside of the membrane. The Ar sweep gas flow is much higher than the sample gas flow, and therefore the sample gas is almost completely replaced by Ar gas (>99.99%). Any particles in the sample gas do not pass through the membrane, but rather remain inside the membrane tube. Consequently, the particles are carried from the GED in the Ar gas stream, which can be directly introduced into the Ar plasma of the ICP-MS and analyzed.

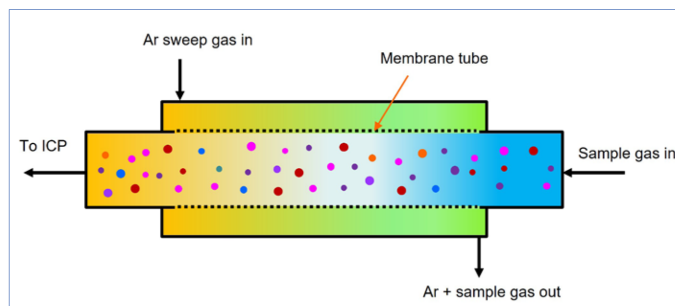

Figure 1. Schematic diagram of GED membrane.

For quantitative GED analysis, metal standard aerosol generation (MSAG) is used. For this approach, a few µL/min of aqueous elemental standard solution is introduced into a special nebulizer with a 0.3 L/min of Ar nebulizer gas. Since the amount of the standard solution introduced is less than the water saturation amount at this Ar gas flow, 100% of the aerosol can be introduced into the plasma of the ICP-MS. As a result, an absolute amount of standard solution introduced into the plasma can be calculated and the sensitivity factor in ag/count can be used for the quantitation. When ICP-MS analysis is carried out on the transient signal, the atomic weight of a particle that corresponds to the diameter of the particle can be obtained. For this application, it is imperative to use an ICP-MS platform that is able to operate at exceptionally low dwell times (<100 µs) in order to accurately characterize the transient signal as this ensures accurate particle counting and particle sizing events.

This paper describes the analysis of metallic impurities in HCl gas by GED with MSAG coupled to PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS.

Instrumentation

There are two models of GED which can be used in the analysis of special gases for semiconductor manufacturing: the GED_SEMI has six gas inlet lines and the GED_LAB has only one gas inlet line. In this experiment, the GED_LAB was used for the analysis of HCl. Figure 2 represents the schematic of MSAG-GED-ICP-MS used in this experiment. The outlets of GED and MSAG were directly inserted into the torch injector of the NexION 5000 ICP-MS. In the case of HCl sample gas, this can be introduced into the plasma with or without a filter, and with or without the GED membrane. For particulate analysis of HCl gas, the GED membrane was used without the filter, and the filter line was used to determine whether the particles came from the sample gas or not. For gaseous impurity analysis, the GED was bypassed, the sample gas was diluted with Ar gas and then introduced into the plasma of the ICP-MS. The Dual Syringe MSAG was used for quantitation, and an acid blank as well as a multi-element standard solution were introduced by means of two syringes of MSAG. The acid blank:standard solution ratio was altered, but the total amount was fixed at 3 µL/min during the experiment.

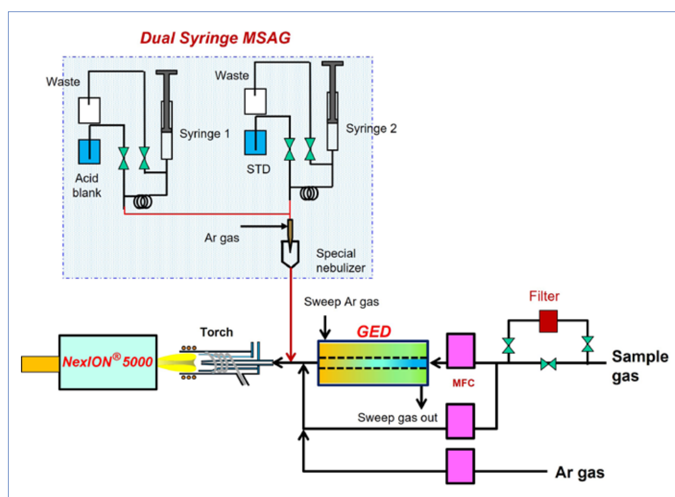

Figure 2. Schematic diagram of MSAG-GED-ICP-MS system.

Experimental

Reagents and Samples

A 10 ppb stock standard solution for ICP-MS calibration was prepared in 0.5% HNO_3 from a 10 ppm multi-element standard solution (XSTC-622B, SPEX CertiPrep, New Jersey, USA). TAMAPURE AA-100 HNO3 (Tama Chemicals Co., Ltd., Kanagawa, Japan) was used for acidifying the standard solution and for a 0.5% HNO_3 acid blank.

The deionized water (DIW) used was the Puric ω (Organo Corp., Tokyo, Japan) and all chemicals were prepared in an ISO Class 5 clean draft.

HCl gas in a 10 L cylinder and gas pressure regulators were purchased from a gas company in Japan.

Instrumental Conditions

Table 1 shows the operating conditions of GED for HCl gas analysis.

Table 1. GED_LAB Parameters.

Parameter	Value
Sample Gas Flow For Particle Analysis (mL/min)	600
Sweep Ar Gas Flow (L/min)	4
GED Cell Pressure (KPa)	9.8
MSAG Nebulizer Ar Gas Flow (mL/min)	300
MSAG 10 ppb Standard Solution Flow (µL/min)	1
Ar Makeup Gas Flow (mL/min)	120
Sample Gas Flow For Direct Analysis (mL/min)	0.2
Ar Dilution Gas Flow (mL/min)	830

Table 2 shows the instrumental conditions of the NexION 5000 Multi-Quadrupole ICP-MS. A single hot plasma condition was used to achieve better decomposition of gases in the plasma, and NH_3 and O_2 reaction gases were used in order to overcome interference issues.

Table 2. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Torch	Demountable 2 mm i.d. Pt injector
RF Power	1500 W Hot Plasma
Measuring Time	0.45 Sec for Direct Gas Analysis (Quantitative Analysis Method)
Number Of Replicates for Direct Gas Analysis	Three Times
Cell Modes	Standard and Reaction
Cell Gases	NH_3 and O_2

Results and Discussion

Gas exchange efficiency was investigated for HCl gas using the GED_LAB model. Figure 3 represents the relationship between the sample gas flow and the signal intensity of the gas detected by ICP-MS with different sweep gas flows of the GED.

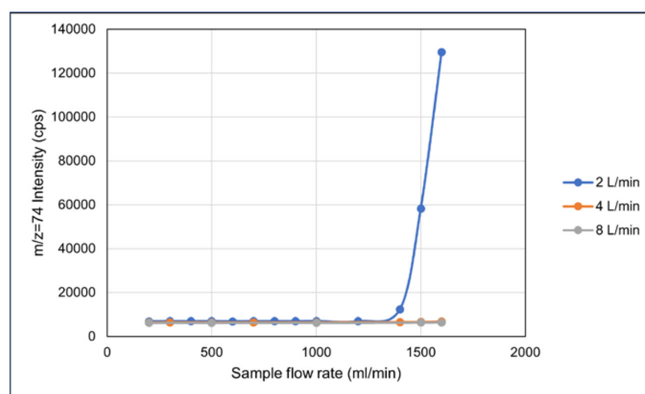

Figure 3. Gas exchange efficiency for HCl gas.

In order to ensure proper gas exchange efficiency, the Ar sweep gas flow was fixed at 4 L/min during the experiment and the HCl gas flow introduced to GED was at 600 mL/min.

Particle analysis in HCl gas was carried out using the GED_LAB model. The dwell time was set to 1 msec and nano analysis mode on Syngistix™ for ICP-MS software was used. When the ICP-MS background is 1000 cps, it should give 1 count per every 1 msec dwell time. Figures 4-1 and 4-2 represent the time chart of the elements. The upper graphs are with the filter and the lower graphs are without the filter. When there were particles in a gas that could be trapped by the filter, the background with the filter was almost 0 or 1 count, i.e. ^{24}Mg, ^{40}Ca, ^{48}Ti, ^{51}V, ^{59}Co, ^{98}Mo, ^{184}W and ^{208}Pb. It was clear that many particles in the HCl gas could be detected without the filter. Some elements – ^{31}P, ^{75}As, ^{120}Sn, and ^{121}Sb – showed higher backgrounds even with the filter which seemed to be due to gaseous impurities. At the bottom right of Figure 4-2, the results of Mo with and without the filter as well as Ar gas without the filter are shown. Some particles were trapped by the filter. However, there was a difference between the filtered HCl and the Ar without the filter. The obtained readings of 1 or 2 counts with the filtered HCl were higher than those without the filtered Ar gas. These 1 or 2 count signals might be gaseous impurities or very small particles that passed through the filter. Figure 5 shows the transient signal

of Fe over the course of three hours. A higher amount of Fe particles were detected right after opening the valve of the gas cylinder (^{56}Fe without filter ①) and the signals varied over the course of several hours (^{56}Fe without filter ②), and were found to stabilize after three hours (^{56}Fe without filter ③). When HCl gas was passed through the filter, the signals dropped significantly (^{56}Fe without filter ④). The cause of the signal instability was thought to be due to the vaporization of liquified gas in the gas cylinder. As the HCl gas was consumed, the liquid was vaporized to keep the vapor pressure at liquid temperature, and the temperature of the liquid was reduced by the heat of vaporization. When the consumption of the gas is higher than the speed of vaporization, the liquid boils and particles in the liquid might be released into the gas phase. Some other elements, such as Na, K, Ti and Sn, showed similar instability. According to the sensitivity obtained by the standard addition from MSAG to HCl gas and density of Fe, i.e. 7.874 g/mol, 1 count intensity was equivalent to 5.7 nm diameter of Fe.

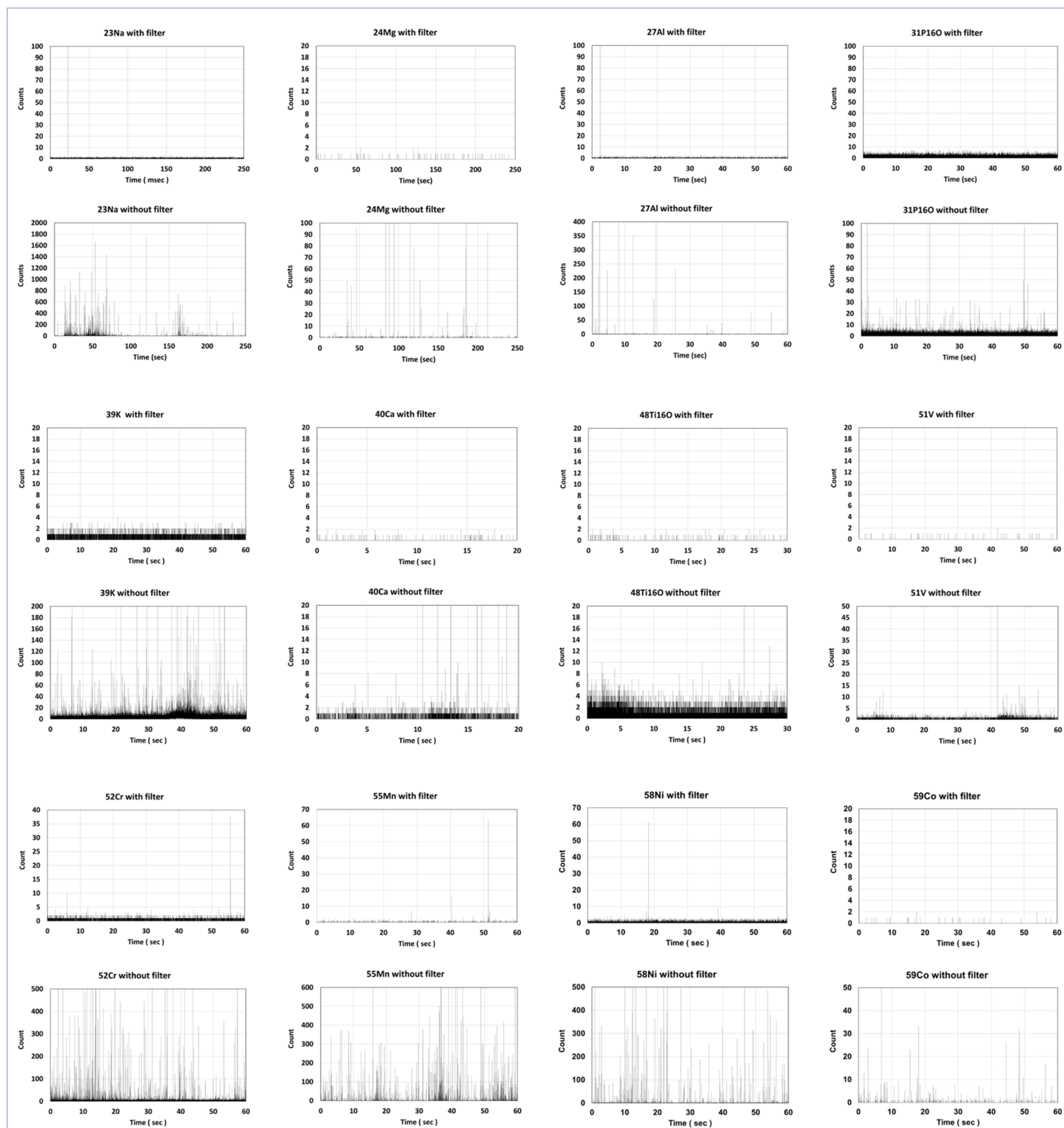

Figure 4-1. HCl gas. Upper: with filter; Lower: without filter.

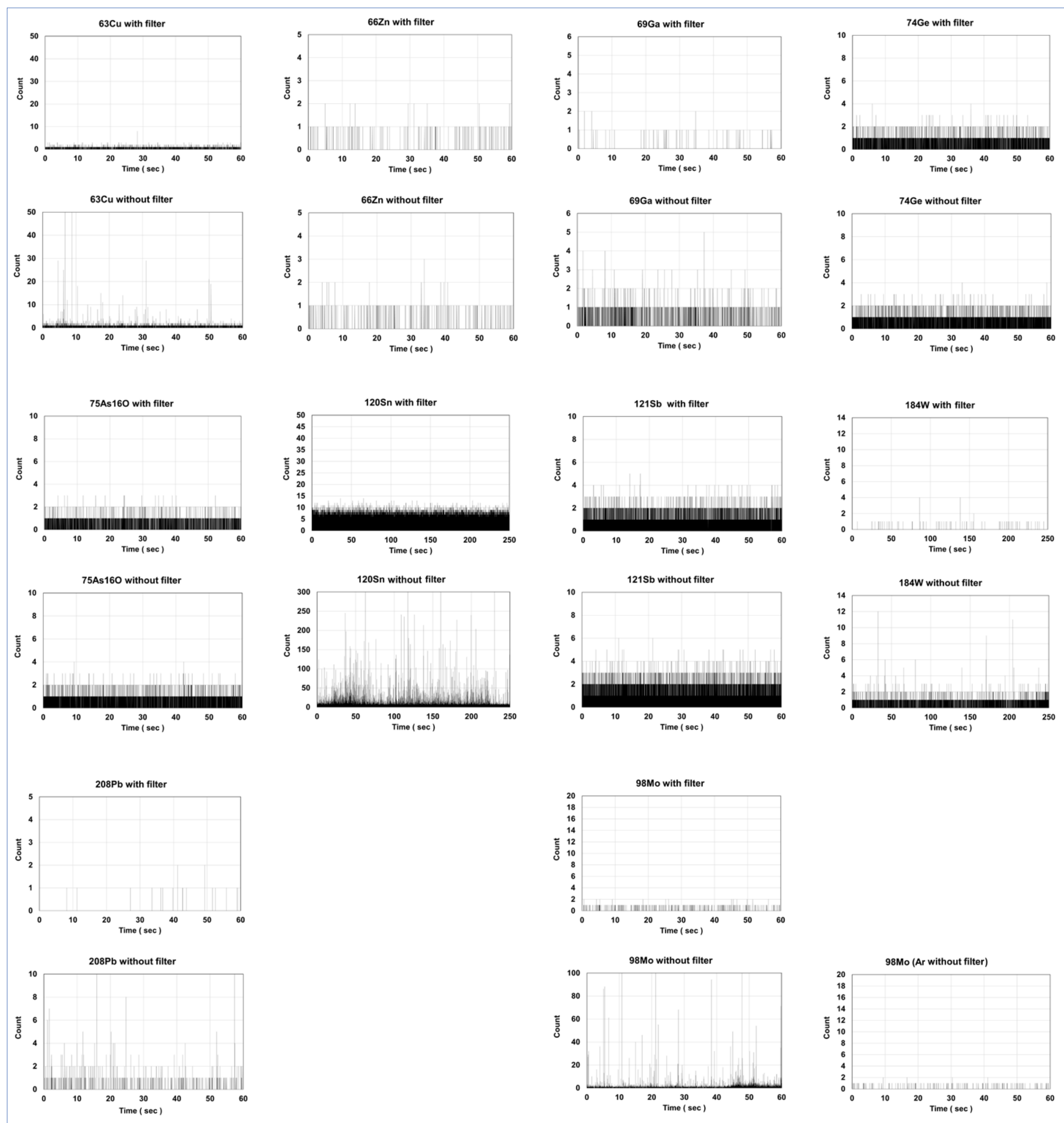

Figure 4-2. HCl gas. Upper: with filter; Lower: without filter; Lower right of ^{98}Mo: Ar gas blank.

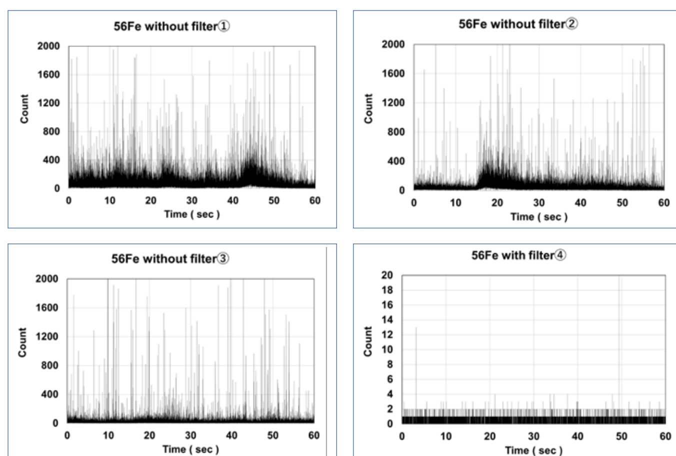

Figure 5. Fe in HCl gas: ①1 After opening cylinder valve; ② One hour later; ③ Three hours later; ④ With filter.

Since some gaseous impurities were detected by GED-ICP-MS, HCl gas was analyzed directly without using GED. Only 0.2 mL/min of gas was introduced with the Ar gas (total gas flow to the torch injector was 1.25 mL/min). Figure 6 shows the trend of intensity. After opening the gas cylinder valve, Sn and Sb signals initially increased, decreased and then stabilized after one hour. Ge and As signals increased gradually and stabilized after 2.5 and 4 hours, respectively.

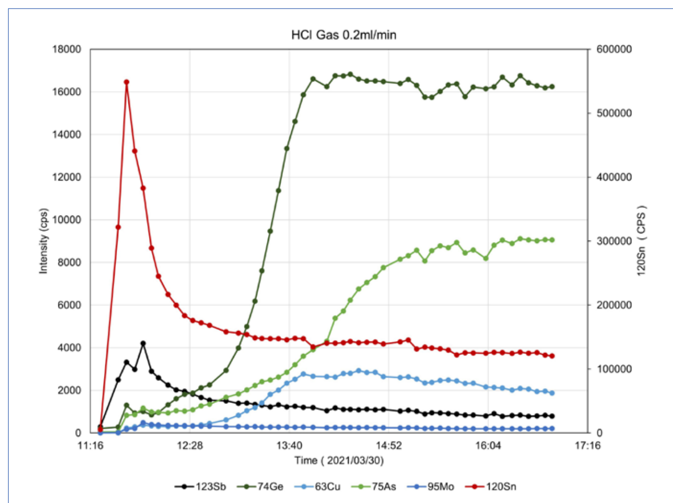

Figure 6. Trend of elements in HCl gas by direct analysis.

Table 3 shows the results of HCl gas analysis for particle and gaseous impurities. The concentration was calculated using method of standard addition by MSAG. The intensities of the standard added to the Ar blank gas and HCl gas were quite different: some elements, such as Li, Na, Mg, Al, Ti, As, Mo and Ag, showed higher sensitivity in HCl than Ar gas, while other elements, such as P, V, Zr, Cd and Pb, showed lower sensitivity in HCl than Ar gas. The reason for the difference is still unknown, but it was necessary to use the method of standard addition in order to get accurate results. Moreover, the use of lower Ar gas flows for MSAG was also considered essential in order to have higher sample gas flows so that the Ar gas flow for the MSAG was fixed at 300 mL/min.

When scanning mode was used, all background counts were accumulated, and it was impossible to discern a few counts of signal. On the other hand, the transient signal mode could easily distinguish a few counts of the signal. The particle analysis using GED clearly showed some particles of Mg, Al, K, Ca, Cr, Mn, Co, W and Pb, as shown in Figures 4-1 and 4-2, but the direct HCl gas analysis with 0.45 sec integration time using the scanning mode could not detect these elements. The transient signal mode was also tested for the direct HCl gas analysis, but no particle signals were observed because the gas flow was too low, i.e. 0.2 mL/min and particles might be trapped in the sampling gas line.

On the other hand, GED could not detect gaseous impurities such as P, V, Ge, As, Sn and Sb, whereas the direct HCl gas analysis mode could detect them.

The MS/MS and Mass Shift scan modes of the NexION 5000 ICP-MS allow only on-mass ions to enter the quadrupole Universal Cell, preventing side reactions between Cl and NH ions with other ions which were in the sample. This enables completely interference-free ICP-MS analysis.

The GED software was integrated with the NexION 5000's Syngistix™ for ICP-MS software, allowing to access Dataset and Method files of Syngistix software, delivering a fully automated solution for direct analysis of metallic impurities in gas.

Table 3. Results of HCl Gas.

Element	Masses	Particle Using GED		Direct Gas					
		Integration Time (sec)	Conc. (ng/kg)	Integration Time (sec)	Ar (cps)	Ar + STD (cps)	HCl (cps)	HCl + STD (cps)	Conc. (ng/kg) HCl - Ar
Li	7/7	250	0.005	0.45	0	30,852	0	55,102	N.D.
Na	23/23	250	0.12	0.45	2	62,657	9	99,699	15
Mg	24/24	250	0.008	0.45	0	42,882	0	57,544	N.D.
Al	27/27	60	0.017	0.45	10	60,090	6	69,112	N.D.
P	31/47	60	1.5	0.45	2,411	38,538	2,586	31,380	14,000
K	39/39	60	1.2	0.45	37	111,032	33	120,730	N.D.
Ca	40/40	60	0.15	0.45	9	97,360	9	106,194	N.D.
Ti	48/64	60	0.72	0.45	1	37,861	7	44,084	27
V	51/51	60	0.073	0.45	0	74,564	292	68,807	680
Cr	52/52	60	1.74	0.45	581	96,456	67	96,151	N.D.
Mn	55/55	60	0.31	0.45	2	167,237	2	168,823	N.D.
Fe	56/56	60	33	0.45	32	136,656	3,876	140,699	4,500
Ni	58/58	60	0.46	0.45	29	58,403	66	56,978	48
Co	59/59	60	0.006	0.45	0	108,607	1	110,188	N.D.
Cu	63/63	60	0.03	0.45	8	56,121	1,872	58,996	8,700
Zn	66/66	60	0.003	0.45	6	19,915	31	17,662	530
Ga	69/69	60	0.009	0.45	3	127,200	27	115,844	23
Ge	74/74	60	0.03	0.45	223	133,279	12,156	126,898	44,000
As	75/91	60	0.27	0.45	51	8,850	9,055	18,124	320,000
Sr	88/88	60	N.D.	0.45	0	221,504	1	225,230	N.D.
Zr	90/106	-	-	0.45	0	369,977	0	336,718	N.D.
Mo	98/98	60	0.46	0.45	4	43,826	11,350	63,485	51,000
Ag	107/107	-	-	0.45	0	60,160	0	71,920	N.D.
Cd	111/111	250	N.D.	0.45	1	100,486	0	87,879	N.D.
Sn	120/120	250	N.D.	0.45	5,506	53,986	120,436	(*1) 131,845	180,000
Sb	121/121	60	0.23	0.45	370	58,668	1,116	58,625	3,100
Ba	138/138	250	N.D.	0.45	0	106,331	0	128,845	N.D.
W	184/184	250	0.051	0.45	0	36,557	0	40,978	N.D.
Pb	208/208	60	0.007	0.45	0	121,929	0	103,510	N.D.

N.D.: not detectable

Conclusion

MSAG-GED-ICP-MS opens up new opportunities for the analysis of metallic impurities in gases, offering a powerful analytical solution which meets the demanding needs of the semiconductor industry. Particle measurement by GED using short dwell times allowed the detection of a few nm of particles in the HCl gas. When the particles were measured with the filter, some particle signals were still detected. The source of particles with the filtered HCl gas was still unknown and further investigation is needed.

The GED_SEMI model has six gas inlet lines that can be switched automatically by the GED software. This allows the GED_SEMI system to be used as an inline analytical tool for the analysis of metallic impurities in gases used in semiconductor manufacturing processes.

The GED membrane has also been tested for other gases such as Cl_2, NH_3, HF, NF_3, SF_6, CO_2 and SiH_2Cl_2, and the results will be presented in a future publication.

The new opportunity to combine these capabilities with the NexION 5000 ICP-MS' unique multi-quadrupole technology, fast scanning and exceptionally low background equivalent concentrations in hot plasma provides unprecedented benefits for the semiconductor and electronics industry.

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