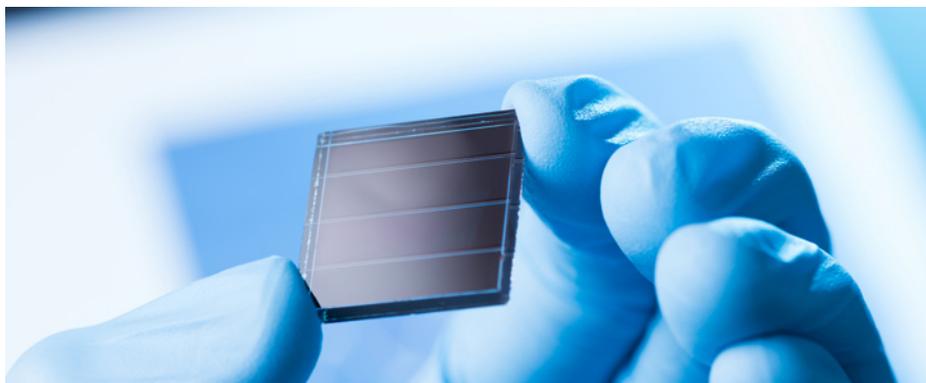


# Direct Analysis of Metallic Impurities in SiC and GaN Wafers by LA-GED-MSAG-ICP-MS/MS

Automated analysis using Agilent 8900 ICP-QQQ with Laser Ablation, Gas Exchange Device, and Metal Standard Aerosol Generation



## Authors

Koshi Suzuki, Tatsu Ichinose,  
and Katsu Kawabata  
IAS Inc., Hino, Tokyo, Japan

Kazuhiro Sakai  
Agilent Technologies, Inc.,  
Hachioji, Tokyo, Japan

## Introduction

Semiconductor devices are used in many electronic items and are increasingly indispensable in the electric vehicle (EV), communication, and data storage sectors. Research is also underway to develop energy storage systems to manage energy generated from intermittent renewable sources, such as solar, wind, and tidal. Effective energy storage systems require fast, high-power semiconductor devices to convert alternating current (AC) to direct current (DC) or DC to AC.

Power-semiconductor devices are often fabricated on wafers made from wide-bandgap (WBG) materials, such as silicon carbide (SiC) and gallium nitride (GaN) rather than silicon (Si). These alternative, non-Si, semiconductor materials are becoming increasingly popular in power electronics because of their higher breakdown voltages and better temperature tolerance. As with Si-based semiconductors, the electrical characteristics of these alternative materials are highly dependent on the purity of the substrate material. To achieve the required performance and quality of the power-devices, the level of contaminants in the SiC and GaN wafer substrates must therefore be closely monitored using a suitable analytical technique.

Total reflection X-ray fluorescence (TRXRF) has been commonly used for the analysis of metallic impurities in Si wafers because it is a non-destructive technique. However, TRXRF can only measure the surface of solid materials and its detection limit (DL) capabilities are insufficient to meet the requirements of most semiconductor applications. To improve the DLs of TRXRF, a preconcentration approach using vapor phase decomposition (VPD) can be used. Typically, VPD uses hydrofluoric acid (HF) vapor to decompose the oxide layer or surface film, such as SiN, on a Si wafer. Metallic impurities are released from the film or oxide layer and remain on the wafer surface, where they are collected by a recovery solution held by a scan nozzle. The recovery solution is placed back onto the wafer surface and dried, concentrating the metals from the whole wafer into a small spot for analysis by TRXRF. The VPD technique improves the DLs achievable by TRXRF by about 700 times for a 12 inch (12") wafer, although the decomposition of the surface layer means that the VPD-TRXRF can no longer be considered as a non-destructive technique.

VPD sample preparation can also be used with a trace element analysis technique such as inductively coupled plasma-mass spectrometry (ICP-MS). Once the surface layer has been decomposed and the VPD recovery solution has been collected, the liquid droplet can be transferred directly to the ICP-MS for analysis. VPD-ICP-MS provides 100 times better DLs than VPD-TRXRF and is also much easier to automate (1).

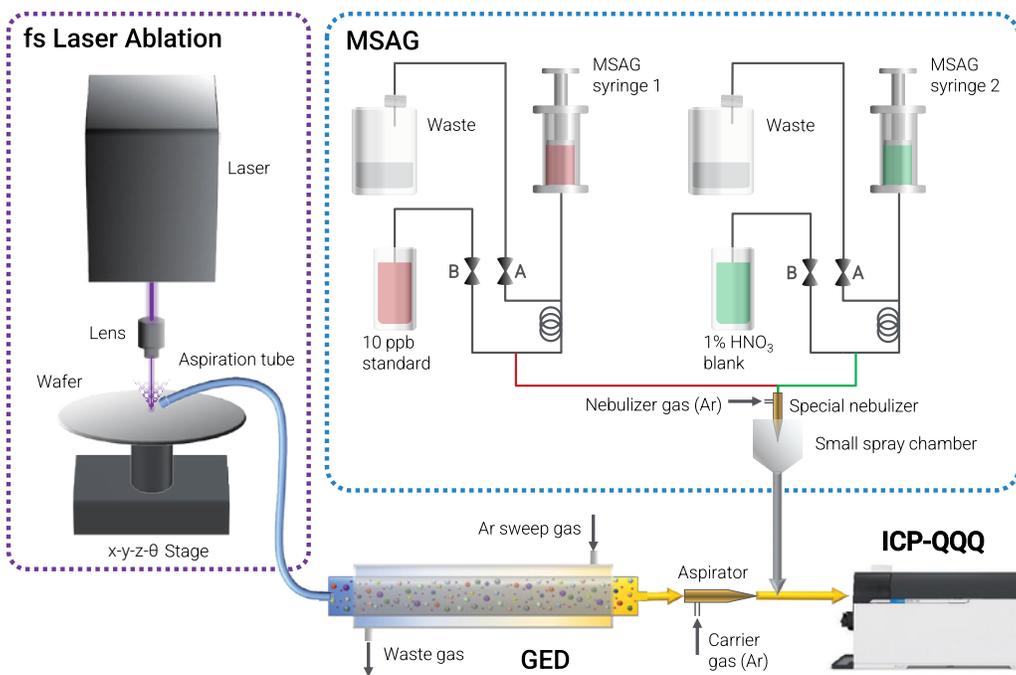
Because of its advantages, VPD-ICP-MS is widely used for the analysis of metallic impurities in Si wafers at many major Si-based semiconductor fabrication facilities (FABs). HF vapor alone is suitable for decomposing native oxide and thermally oxidized SiO<sub>2</sub> layers and certain thin films. By adding ozone gas to the HF vapor during the VPD process, the technique can also be applied to etching of epitaxial Si, poly-Si layer, or the unoxidized, pure Si substrate, allowing the analysis of metallic impurities in the bulk Si wafer substrate. However, VPD-ICP-MS is not suitable for the analysis of elemental impurities in alternative wafer materials such as SiC and GaN, because these materials cannot be decomposed by the HF vapor.

Laser ablation (LA)-ICP-MS is a widely used technique for solid sample analysis and could be applied to the direct analysis of multiple elements in SiC and GaN wafers. However, there are two major issues with using conventional LA-ICP-MS systems for accurate quantitative analysis of trace contaminants in semiconductor wafers:

1. Solid samples for LA must be placed in an enclosed ablation chamber or "cell" to exclude air and to ensure that the particles generated by the ablation can be collected by a carrier gas and transferred to the ICP-MS for analysis. But even the largest ablation chambers used with commercial laser ablation systems are not large enough to hold a whole 12" wafer.
2. Quantitation of solid samples is more difficult due to the limited availability of matrix matched solid standards. Well-characterized reference materials (RMs) are available for some solid materials, such as glass and certain alloys. These RMs can be used as solid calibration standards for LA-ICP-MS. However, the ablation process varies for different materials, so calibration standards need to be closely matched to the samples being analyzed. The number and size of the particles generated by LA depends on the laser wavelength and the properties of the material being ablated. Any variation in the ablation process between the standards and samples would affect the accuracy of the quantitative results using LA-ICP-MS.

For many years, researchers have tried to overcome the lack of solid standards by simultaneously aspirating liquid calibration standards – introduced using a conventional or desolvating nebulizer – while ablating the sample (2). But the exact amount of standard added in the liquid aerosol is difficult to calculate, so this approach is prone to errors in quantitation. The addition of a liquid standard also does not compensate for variations in the ablation rate, so this approach still requires correction using an internal standard or matrix element.

To overcome these two issues, a new LA technique has been developed by IAS Inc (Hino, Tokyo, Japan) which uses a femtosecond (fs) LA system, Gas Exchange Device (GED), Metal Standard Aerosol Generation – Dual Syringe (MSAG\_DS), and triple quadrupole ICP-MS (ICP-QQQ with MS/MS) for direct analysis of whole wafers. Figure 1 shows a schematic of the LA-GED-MSAG-ICP-MS/MS technique.



**Figure 1.** Schematic diagram of LA-GED-MSAG-ICP-MS technique.

As shown in Figure 1, the LA system used for LA-GED-MSAG-ICP-MS does not require an enclosed ablation chamber. Instead, the wafer is mounted on an x-y-z-θ (rotation) stage, and the ablation occurs in a clean, particle free, air environment. Sample material generated by the ablation is extracted into a transfer tube and passed through the GED where the air is exchanged for Ar carrier gas before being introduced to the plasma of the ICP-MS.

The GED uses a glass membrane that exchanges air and Ar gas efficiently (>99.99%), based on the partial pressure of each gas (3). The pressure on the Ar sweep gas side of the membrane is slightly higher than on the air side, so particles cannot pass through the membrane and be lost in the GED. When Ar gas is supplied to the aspirator, the particles generated by the ablation are drawn up into the aspiration transfer tube and carried through the GED to the ICP-MS.

Calibration of the solid sample analysis is performed by the MSAG, which adds vaporized liquid calibration standards to the dry gas flow carrying the ablated sample material. The MSAG delivers a few  $\mu\text{L}/\text{min}$  of an aqueous solution to a specially designed nebulizer that operates with 0.3 L/min of Ar nebulizer gas flow. When the total solution flow introduced to the nebulizer is less than the water saturation level, complete vaporization of the aerosol occurs and practically 100% of the solution is passed to the plasma of the ICP-MS. The saturated water vapor pressure for a 0.3 L/min Ar gas flow at 20 °C is around 5  $\mu\text{L}/\text{min}$ , so, at a total flow rate of <5  $\mu\text{L}/\text{min}$ , the solution vaporizes completely.

At higher solution flow rates, vaporization would be incomplete and some aerosol could be trapped in the spray chamber causing solution loss. The use of MSAG with “total consumption” nebulization allows the exact amount of solution, and therefore the amount of each analyte element in each standard addition, to be calculated.

The dual syringe MSAG is connected to the gas transfer line between the aspirator and ICP-MS torch. The introduction of a few  $\mu\text{L}/\text{min}$  of water vapor to the plasma increases the ICP-MS sensitivity compared to dry plasma conditions. But the sensitivity enhancement depends on the amount of water vapor, so two syringes are used to maintain the same total liquid flow as the volume of standard added is varied, thereby ensuring consistent ICP-MS sensitivity. The dual syringe MSAG supplies a mixed metal standard in 1%  $\text{HNO}_3$  solution from one syringe and a 1%  $\text{HNO}_3$  blank solution from the second syringe. The ratio of the standard and blank solution is changed by the two syringes, which enables quantitation by the method of standard addition (MSA). The total flow rate of the solution introduced to the nebulizer is fixed at 3  $\mu\text{L}/\text{min}$  to ensure complete vaporization and prevent droplet formation.

The combination of LA, GED, and dual syringe MSAG with ICP-MS/MS enables the direct analysis of 12" wafers. MSA calibration by addition of liquid standards provides a flexible and highly accurate method for the quantitative analysis of contaminants in the wafers, without requiring matrix-matched solid standards.

A fully automated model of the LA-GED-MSAG-ICP-MS is available that includes two Front Opening Unified Pod (FOUP) load ports, a wafer transfer robot, and aligner. When a FOUP is loaded and an automated method is set from within the software, a wafer will be analyzed automatically. There are several preset LA methods or “patterns” designed for wafer analysis, such as full, line, block, depth profile, and multi-spot. The “full” method ablates the entire surface of a wafer equally just by setting the total ablation time. The line method ablates a straight line from point A to point B while the x-y-z-θ stage moves the sample in the x direction and the galvo mirror moves the ablation site over a specified width in the y axis. The block method is similar to the line method, but only the galvo mirror is used to ablate a specified two-dimensional (2D) area or block. After the ablation is finished, the x-y-z-θ stage moves the sample to a new ablation site, and the block ablation is repeated. The depth profile method is similar to the block method, but the block ablation is repeated at the same site after a specified time delay. The multi-spot method ablates multiple specified spots of a specified size.

In this study, LA-GED-MSAG coupled to an Agilent 8900 ICP-QQQ was used for the quantitative analysis of contaminant elements in Si, SiC, and GaN wafers. The technique was also investigated for the analysis of discrete particles on the wafer surface. For the bulk quantitative measurements, wafers were analyzed using the line ablation method, while the multi-spot method was used for the measurement of particles and nanoparticles.

## Experimental

### Reagents and samples

For the calibration of the ICP-MS by the dual syringe MSAG, a 10 ng/mL (ppb) multi-element standard solution was prepared in 1% HNO<sub>3</sub> from a 10 µg/mL (ppm) stock standard (XSTC-622B, SPEX CertiPrep, NJ, USA). For the matrix elements, Si and Ga, 10 ppm standard solutions were prepared in 1% HNO<sub>3</sub> from 1,000 ppm single element stock standards (SPEX CertiPrep). The 1% HNO<sub>3</sub> acid blank and standard solution diluent were prepared using TAMAPURE AA-100 HNO<sub>3</sub> (Tama Chemicals Co., Ltd., Kanagawa, Japan). De-ionized water (DIW) was produced using the Puric ω system (Organo Corp., Tokyo, Japan). All chemicals were prepared in an ISO Class 5 clean hood.

Research grade and dummy grade wafers of Si, SiC, and GaN were bought commercially. Dummy wafers are used within the industry for wafer production processes, process condition verification tests of manufacturing equipment, performance evaluations, and inspections. In general, research grade wafers contain higher levels of metal contaminants than dummy grade wafers.

### Instrumentation

The 8900 ICP-QQQ (#200, Semiconductor configuration) was fitted with the standard quartz torch with 2.5 mm injector and standard Pt-tipped sampling cone. The standard s-lens was replaced with the optional m-lens (Agilent part number G3666- 67500) and optional Pt-tipped, Ni-based skimmer cone for m-lens (p/n G3666-67501). The m-lens is specially designed to minimize elemental background from the interface cones under hot plasma conditions, which is a critical factor when ultratrace level analytes are measured in high matrix samples.

To ensure that the lowest DLs were achieved for the 30 analytes included in this study, a multitune method was set up in the Agilent ICP-MS MassHunter instrument control software. This approach allows the tuning conditions to be optimized for the removal of different types of interferences, while maintaining sensitivity for each analyte. The MS/MS configuration of the 8900 provides effective removal of spectral overlaps on analytes, ensuring low DLs and accurate data. In this work, ammonia and hydrogen reaction cell gases (with helium buffer gas) were used for the most effective control of potential overlaps on the analytes being measured. 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 hot plasma conditions were used for all ICP-MS reaction gas modes. Instrument operating conditions and acquisition parameters are given in Table 1.

The 8900 ICP-QQQ was tuned during the ablation of a sample wafer and addition of a 10 ppb standard solution at 1 µL/min plus 2 µL/min 1% HNO<sub>3</sub> blank solution from the dual syringe MSAG.

**Table 1.** LA-GED-MSAG-ICP-MS operating parameters.

Device	Parameter	Value
Femtosecond Laser with galvanometer (galvo) mirror	Frequency (kHz)	10
	Pulse duration (fs)	290
	Wavelength (nm)	257 ± 2
	LA pattern	Line
	Galvo mirror scan speed (mm/sec)	100
	Galvo mirror jump speed (mm/sec)	1,000
	Aspirator Ar gas flow (L/min)	0.14
GED	Sweep Ar gas flow (L/min)	4
	GED cell pressure (KPa)	9.8
MSAG_DS	MSAG nebulizer Ar gas flow (L/min)	0.4
	MSAG solution injection flow (µL/min)	3
	MSAG stock standard solution concentration (ppb)	10
ICP-MS	Makeup Ar gas flow (L/min)	0.45
	RF power (W)	1,500
	Sampling depth (mm)	8
	10% NH <sub>3</sub> /He gas flow (%), He gas flow (mL/min)	10–20%, 2
	H <sub>2</sub> gas flow, He gas flow (mL/min)	9, 1

## Results and discussion

### Analysis of spiked Si wafer

A 5  $\mu\text{L}$  droplet of a 0.1 ppb mixed standard solution was pipetted onto the surface of a 12" Si wafer mounted on the x-y-z- $\theta$  stage of the femtosecond laser (Figure 2). The droplet was allowed to dry, and the dried spot was then ablated using a combined stage movement and galvo mirror line scan to collect data from the bulk wafer (background) and the entire dried spot. The ablation scan comprised a 5 mm wide ablation path (controlled by the galvo mirror scan) along a 40 mm line (controlled by the stage x-y-z- $\theta$  stage motors). The high speed of the galvo mirror scan (100 mm/s) and the high frequency of the ablation (10,000 shots per second) gave close to instantaneous ablation across the entire 5 mm line width sampled.

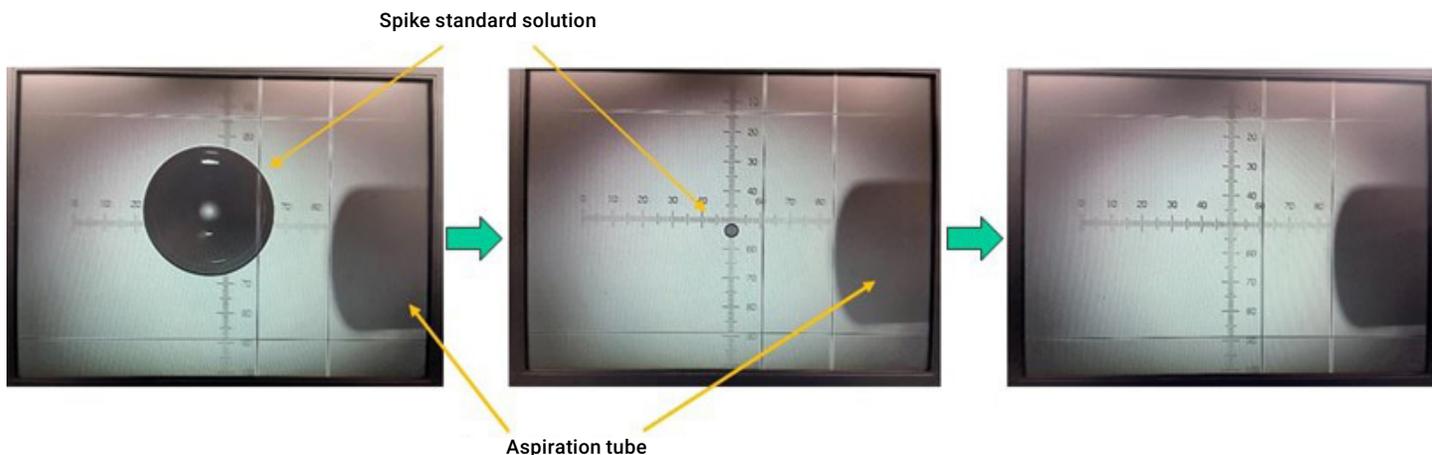
The 30 elements of interest were measured using the time-resolved analysis (TRA) transient signal measurement mode of the 8900 ICP-QQQ with a dwell time of 50 ms per mass and a total sweep time of 1.6022 s. A single  $\text{NH}_3$  reaction gas mode with 10% cell gas flow (1.0 mL/min) was used for all analytes.

Figure 3 shows the TRA time plots of selected elements acquired during the laser ablation of the spiked wafer. After 58 s of acquisition of a gas blank, the ablation was started and the signal of  $^{29}\text{Si}$  quickly rose and remained steady from 58 s until ablation was stopped at 488 s. As the ablation site passed across the dried droplet on the Si wafer surface, the TRA plots for the other elements clearly showed when the signals from the spiked standard solution were ablated and detected by the 8900 ICP-QQQ (between 220 and 240 s).

Short, sharp peaks were observed for most elements because the standard solution dried to a small spot on the wafer, as shown in Figure 2. LA enables analysts to visualize the spatial distribution of contaminant elements, which is a benefit compared to the VPD technique. VPD collects the elements from across the wafer surface, so any spatial information is lost.

Cu and Ag showed noticeably broader peaks compared to most of the other elements. These two elements have a strong affinity for the Si wafer substrate, so adhered to a larger area of the wafer surface as the spike droplet dried. The strong affinity of Cu and Ag (and the noble metals, gold, platinum, palladium, silver, rhodium, and ruthenium) for the Si matrix makes these elements difficult to recover from a Si wafer using the most common VPD recovery solution of  $\text{HF} + \text{H}_2\text{O}_2$ . The data for Cu and Ag therefore illustrates another benefit of the LA approach; LA physically removes material from the wafer surface for analysis, rather than having to rely on a chemical extraction.

The TRA time plot for Sn shows high counts across the entire wafer surface (between 58 and 488 s) indicating Sn contamination in the Si wafer material. The signal peak from the spike droplet can still be seen, however. If a typical 1,000  $\mu\text{L}$  VPD recovery solution was used to collect the elements from the 100 pg/mL (ppt) spike, there would be a 200x dilution (5  $\mu\text{L}$  spike diluted to 1,000  $\mu\text{L}$  recovery droplet). This would mean the concentration of the elements in the recovery solution would be only 0.5 ppt, making it difficult to detect many of the analytes. In contrast, the LA-GED-MSAG-ICP-MS technique can easily detect contaminants distributed throughout the wafer matrix, and discrete, small spot contaminants.



**Figure 2.** Photos of drying standard solution (5  $\mu\text{L}$  of 0.1 ppb) on a Si wafer. The aspiration tube transports the ablated material into the GED.

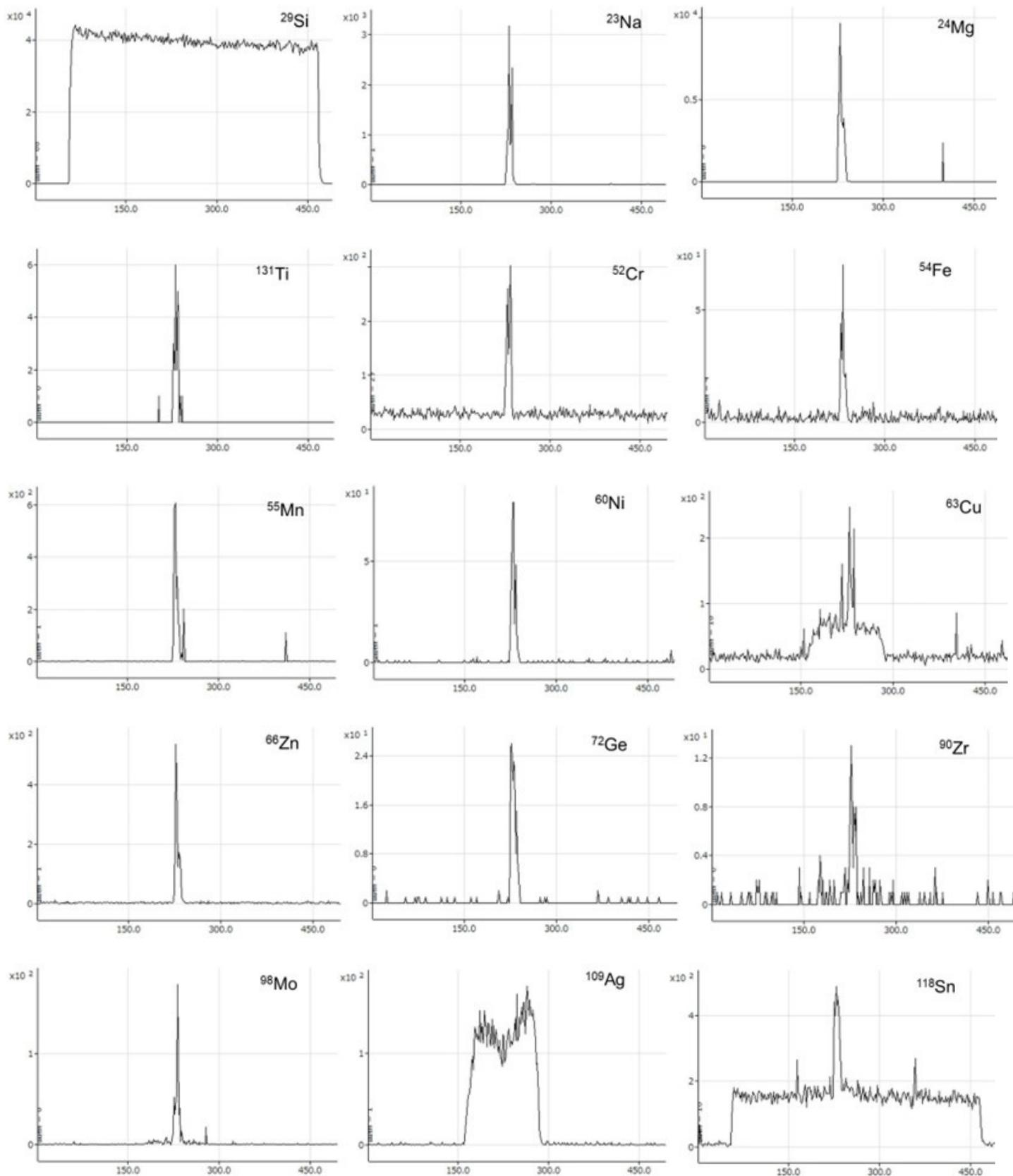


Figure 3. TRA of spiked Si wafer.

## Quantitative analysis of SiC wafers

Two different grades of SiC wafers (research and dummy) were analyzed by LA-GED-MSAG-ICP-MS/MS and the quantitative results calibrated using liquid standard addition are shown in Table 2. The data (three repetitions for each wafer sample) was collected in spectrum mode using an integration time of 0.1 s per mass. Standard addition calibration curves were obtained for the Ar gas blank (no ablation) and the laser ablated SiC wafer using the MSAG to deliver 0, 1.5, and 3  $\mu\text{L}/\text{min}$  of the 10 ppb mixed standard solution to the ICP-MS. The second syringe of the MSAG was used to add an appropriate volume of 1%  $\text{HNO}_3$  blank solution to ensure that the total volume of solution (blank plus 10 ppb mixed standard solution) introduced to the ICP-MS was 3  $\mu\text{L}/\text{min}$  for each of the standard levels.

The ICP-MS intensities showed good correlation coefficients for both the gas blank and SiC wafer ablation. The sensitivity factor for each element was calculated from the slope of the calibration curves in counts per second (cps) and the absolute amount of each element introduced from the dual syringe MSAG was calculated in attograms (ag) per second. The sensitivity achieved for the MSA standards in the gas blank and SiC wafer ablation were similar, confirming the ablated SiC wafer matrix did not cause any significant suppression or enhancement issues during the analysis.

The absolute amount of each element detected in the SiC wafer was calculated from the intensity of the SiC sample ablation with no standard addition (first MSAG syringe set to introduce 0  $\mu\text{L}/\text{min}$  of 10 ppb standard, and second MSAG syringe set to introduce 3  $\mu\text{L}/\text{min}$  of blank 1%  $\text{HNO}_3$ ).

**Table 2.** Measured counts for standard addition spikes in gas blank and with SiC wafer ablation, with quantitative results for contaminant elements in two types of SiC wafers using LA-GED-MSAG-ICP-MS/MS.

Element	Q1/Q2 Masses	Mode	Ar Gas Blank						SiC Research Grade						SiC Dummy Grade		
			STD added flow ( $\mu\text{L}/\text{min}$ )			Corr. Coeff.	Sens. factor (ag/count)	Amount (ag)	STD added flow ( $\mu\text{L}/\text{min}$ )			Corr. Coeff.	Sens. factor (ag/count)	Amount (ag)	Ar blk subt. amount (ag)	Conc. (wt. ppb)	Conc. (wt. ppb)
			0	1.5	3				0	1.5	3						
Li	7/7	No gas	3	39,195	79,088	1.000	6	18	7	39,409	78,542	1.000	6	41	24	1	0.71
Na	23/23	No gas	20	52,604	96,211	0.999	5	97	30	49,466	99,858	1.000	5	139	43	2	3.7
Mg	24/24	No gas	0	39,651	74,212	0.999	6	0	27	37,840	73,800	1.000	6	170	170	10	4.5
Al	27/27	NH3	0	60,733	117,650	1.000	4	0	217	58,893	116,425	1.000	4	867	867	49	28
Si	29/29	NH3	404	6,041	11,807	1.000	44,187	1.79E+07	280,831	-	-			1.24E+10	1.24E+10		
K	39/39	H2	50	111,859	230,973	1.000	2	101	43	107,748	230,706	0.999	2	87	N.D.	N.D.	0.11
Ca	40/40	H2	70	128,770	268,200	1.000	2	121	1,782	128,649	264,564	1.000	2	3,148	3,026	171	20
Ti	48/131	NH3	0	1,865	3,621	1.000	128	0	0	1,889	3,270	0.996	142	0	N.D.	N.D.	N.D.
V	51/51	NH3	0	34,041	64,077	0.999	7	0	3	31,522	61,982	1.000	7	22	22	1	N.D.
Cr	52/52	H2	113	107,972	221,432	1.000	2	237	130	102,254	214,045	1.000	2	282	45	3	2.4
Mn	55/55	H2	7	163,367	336,998	1.000	1	10	57	157,866	331,601	1.000	1	80	70	4	5.6
Fe	54/54	NH3	13	8,338	15,752	0.999	29	383	100	7,880	15,131	1.000	31	3,088	2,705	153	172
Co	59/59	NH3	0	74,539	144,746	1.000	3	0	7	67,428	139,349	1.000	3	23	23	1	1.7
Ni	58/58	NH3	3	18,839	36,661	1.000	13	38	13	39,020	79,153	1.000	6	76	38	2	1.0
Cu	65/65	NH3	17	21,847	43,277	1.000	11	182	204	20,022	41,185	1.000	11	2,311	2,128	120	199
Zn	66/66	NH3	10	16,661	32,917	1.000	14	141	80	15,398	32,222	1.000	14	1,155	1,014	57	8.8
Ge	74/74	H2	3	40,737	83,689	1.000	6	17	0	39,355	84,186	0.999	6	0	0	N.D.	N.D.
As	75/75	H2	3	12,732	24,394	1.000	19	57	117	12,382	25,962	1.000	18	2,101	2,044	115	143
Rb	85/85	H2	3	151,342	322,929	0.999	1	4	0	149,380	317,095	0.999	1	0	N.D.	N.D.	N.D.
Sr	88/88	NH3	0	184,660	371,909	1.000	1	0	27	181,220	358,258	1.000	1	35	35	2	N.D.
Zr	90/90	H2	0	52,937	97,435	0.999	5	0	0	54,053	110,502	1.000	4	0	N.D.	N.D.	N.D.
Mo	98/98	NH3	0	25,133	48,865	1.000	9	0	37	24,809	48,901	1.000	9	351	351	20	13
Ag	107/107	No gas	27	78,530	160,979	1.000	3	78	50	74,116	155,209	1.000	3	150	72	4	6.3
Cd	111/111	NH3	0	17,643	33,594	1.000	14	0	0	16,721	34,170	1.000	14	0	N.D.	N.D.	N.D.
Sn	118/118	NH3	33	43,856	86,267	1.000	5	178	871	44,057	88,639	1.000	5	4,606	4,429	250	383
Sb	121/121	NH3	3	31,206	61,687	1.000	8	23	17	29,768	59,715	1.000	8	132	110	6	1.9
Cs	133/133	NH3	0	168,694	328,687	1.000	1	0	3	163,795	335,443	1.000	1	4	4	0	0.24
Ba	138/138	No gas	0	119,589	245,917	1.000	2	0	13	114,596	244,925	0.999	2	25	25	1	N.D.
W	184/184	No gas	7	33,499	63,470	0.999	7	51	107	33,245	66,549	1.000	7	747	696	39	37
Pb	208/208	No gas	0	74,447	147,791	1.000	3	0	43	75,119	152,950	1.000	3	131	131	7	1.1

Since the elemental sensitivities were similar for the gas blank and SiC wafer ablation, the sensitivity factor measured for the Si liquid standard in the gas blank could be used to calculate the amount of Si ablated from the wafer. The sensitivity factor for Si in the gas blank was 44,187 ag/count, and the Si signal measured in the wafer ablation was 280,831 cps. This gives an absolute amount of Si ablated of 1.24 E+10 ag, which corresponds to 1.8 E+10 ag (0.018 µg) of SiC.

The concentration of each element in weight ppb in the SiC was then calculated relative to the total amount of SiC ablated. For the dummy SiC wafer, only the concentration results are presented in Table 2 due to space limitations.

A TRA acquisition using the 5 mm (width) x 40 mm (length) line ablation was also performed to investigate the distribution of elemental contaminants in the research and dummy grade SiC wafers. Example TRA plots of Na, Cu, and Pb in the two grades of SiC wafer are shown in Figure 4. The data was acquired using a dwell time of 10 ms per mass. The spectra show some spot contamination of Na in the research grade wafer, a relatively high level of Cu contamination over the entire surface of both wafers, and a lower, but still measurable, level of Pb.

### Quantitative analysis of GaN wafers

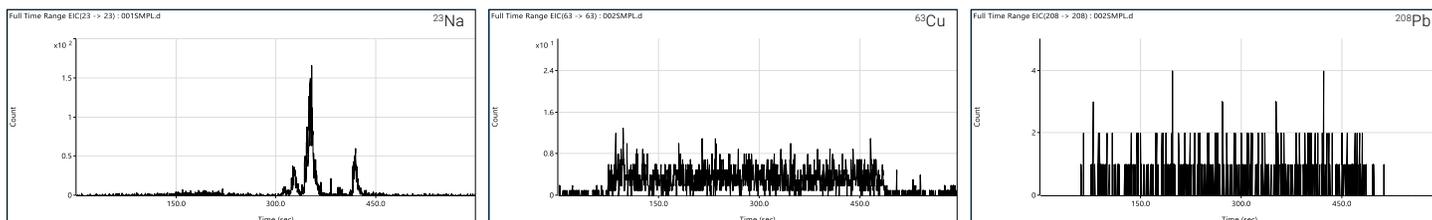
Two types of GaN wafer were analyzed by LA-GED-MSAG-ICP-MS/MS: a single crystal GaN wafer and a GaN film deposited on a Si wafer. The data acquisition conditions used for the analysis of the GaN wafers were the same as those used for the SiC samples. The quantitative results (Table 3) show clear differences between the two GaN wafers, with most elements present at lower concentrations in the GaN film.

When the single crystal GaN wafer was ablated, the relatively heavy matrix caused significant signal suppression, especially for the lighter mass elements. However, using an MSA calibration compensates for matrix effects, so linear calibration curves were generated for the GaN sample and accurate quantitative results could be obtained. The concentration of each contaminant element in the GaN wafers was calculated relative to the total GaN amount ablated, in a similar way to the calculation described previously for the SiC wafer contaminants. The absolute amount of Ga was calculated from the MSA calibration curve while ablating the GaN wafer. The correlation coefficient of Al in the GaN wafer was affected by a high and variable background signal, probably due to Al particle contamination on the wafer surface.

### Single nanoparticle (sNP) analysis

An assessment of Pb particle contamination on the surface of a Si wafer was performed by LA-GED-ICP-MS in single nanoparticle (sNP) analysis mode. TRA plots for continuous measurement of <sup>208</sup>Pb using a 0.1 ms dwell time are shown in Figure 5. With short dwell times, e.g., 0.1 ms, the background signal becomes consistently either 0 or 1 raw count. This low background makes it easier for the (higher) signals arising from single particles or nanoparticles to be clearly distinguished from the background. As shown in the TRA plots in Figure 5, more Pb signal is detected from 10 laser shots than one laser shot. Assuming the Pb signal is from surface particulate contamination, and not from Pb contamination in the Si substrate, the calculated DL of five counts would be equivalent to 50 ag, 1.45 E+05 atoms, or a 10 nm diameter Pb particle.

#### Research Grade SiC



#### Dummy Grade SiC

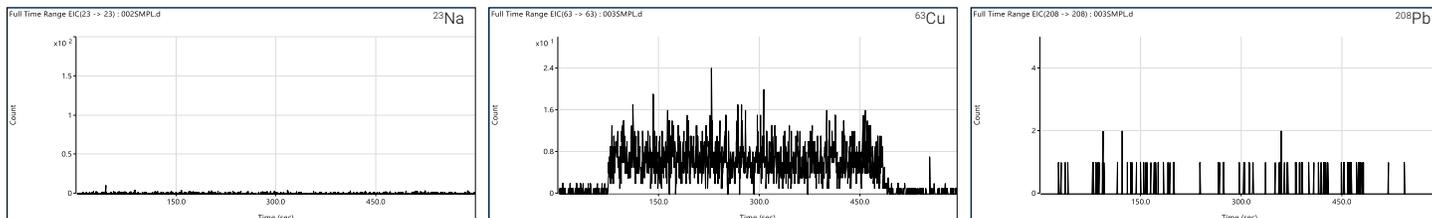
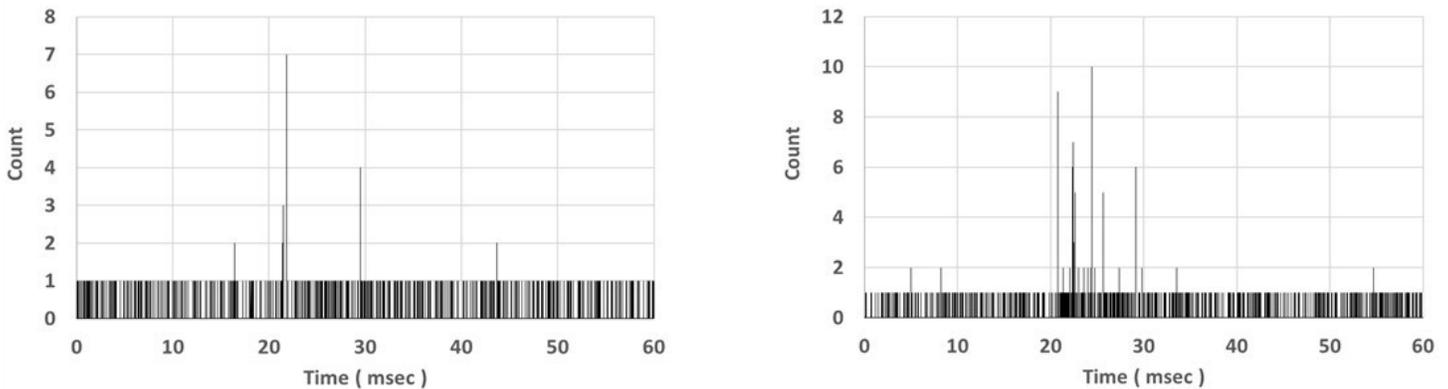


Figure 4. TRA spectra of Na, Cu, and Pb in two different grades of SiC wafer (top: research, bottom: dummy).

**Table 3.** Measured counts for standard addition spikes in gas blank and with GaN wafer ablation, with quantitative results of two types of GaN wafer using LA-GED-MSAG-ICP-MS/MS.

Element	Q1/Q2 Masses	Mode	Ar Gas						GaN Wafer						GaN Layer		
			STD added flow (µL/min)			Corr. Coeff.	Sens. factor (ag/count)	Amount (ag)	STD added flow (µL/min)			Corr. Coeff.	Sens. factor (ag/count)	Amount (ag)	Ar blk subt. amount (ag)	Conc. (wt. ppb)	Conc. (wt. ppb)
			0	1.5	3				0	1.5	3						
Li	7/7	No gas	3	40,239	81,950	1.000	6	18	10	13,918	26,175	0.999	19	191	172	81	153
Na	23/23	No gas	73	50,484	99,757	1.000	5	365	1,081	17,870	35,579	1.000	14	15,633	15,268	7,190	3,200
Mg	24/24	No gas	0	39,564	77,726	1.000	6	0	194	13,357	24,841	0.999	20	3,927	3,927	1,850	195
Al	27/27	NH3	0	56,133	113,292	1.000	4	0	27,289	121,392	87,050	0.627	8	227,821	227,821	107,000	8,630
K	39/39	H2	63	107,814	215,580	1.000	2	146	1,508	30,796	67,804	0.998	8	11,348	11,203	5,270	1,640
Ca	40/40	H2	137	127,174	252,131	1.000	2	271	374	37,333	77,537	1.000	6	2,418	2,147	1,010	2,330
Ti	48/131	NH3	0	1,355	3,017	0.998	165	0	30	457	998	0.998	515	15,462	15,462	7,280	23,800
V	51/51	NH3	0	17,726	40,341	0.998	12	0	3	5,861	12,559	0.999	40	119	119	56	50
Cr	52/52	H2	127	100,797	201,464	1.000	2	315	90	27,540	60,382	0.999	8	745	430	202	44
Mn	55/55	H2	17	142,441	279,734	1.000	2	30	5,654	40,801	85,900	0.997	6	35,153	35,122	16,500	8
Fe	56/56	NH3	70	93,567	182,653	1.000	3	191	1,625	25,911	53,142	0.999	10	15,737	15,546	7,320	868
Co	59/59	NH3	0	64,558	135,866	1.000	4	0	3	19,648	41,460	1.000	12	36	36	17	N.D.
Ni	60/60	NH3	0	15,729	33,248	1.000	15	0	7	4,509	9,627	0.999	52	363	363	171	277
Cu	63/63	NH3	0	40,867	86,785	0.999	6	0	257	11,219	24,484	0.998	21	5,292	5,292	2,490	224
Zn	66/66	NH3	3	14,820	30,208	1.000	17	50	37	4,138	8,925	0.999	56	2,077	2,027	954	1,010
Ga	71/71	No gas	10	7,082	15,040	0.999	33,792	3.38E+05	588,121	684,407	756,411	0.997	3018	1.77E+09	1.77E+09	-	-
Ge	74/74	H2	0	34,708	69,674	1.000	7	0	0	11,043	23,859	0.999	21	0	0	N.D.	N.D.
As	75/75	H2	3	2,670	8,822	0.975	57	170	63	327	1,044	0.966	509	32,040	31,871	15,000	3,020
Rb	85/85	H2	3	126,855	247,073	1.000	2	6	3	46,416	99,847	0.999	5	15	9	4	N.D.
Sr	88/88	H2	0	136,896	262,657	1.000	2	0	7	52,418	107,894	1.000	5	32	32	15	22
Zr	90/90	H2	0	23,097	58,104	0.993	9	0	0	14,902	26,108	0.997	19	0	0	N.D.	N.D.
Mo	98/98	No gas	0	22,345	40,835	0.999	12	0	23	11,590	21,747	0.999	23	528	528	249	30
Ag	109/109	NH3	27	70,575	141,850	1.000	4	95	33	22,141	45,932	1.000	11	359	264	124	N.D.
Cd	111/111	NH3	0	13,491	26,641	1.000	19	0	3	4,358	8,979	1.000	56	167	167	78	
Sn	118/118	NH3	43	36,044	71,381	1.000	7	301	1,084	13,959	28,364	0.999	18	19,825	19,524	9,190	3,000
Sb	121/121	NH3	0	23,438	48,165	1.000	10	0	3	8,341	18,001	0.999	28	83	83	39	N.D.
Cs	133/133	NH3	7	141,286	285,532	1.000	2	12	3	54,187	111,629	1.000	4	13	1	1	N.D.
Ba	137/137	H2	17	11,180	21,413	1.000	23	396	3	5,126	10,068	1.000	50	149	0	N.D.	N.D.
W	184/184	No gas	7	27,773	48,313	0.996	10	72	257	16,852	30,351	0.998	17	4,261	4,188	1,970	N.D.
Pb	208/208	NH3	0	37,024	74,482	1.000	7	0	220	14,149	29,847	0.999	17	3,705	3,705	1,740	N.D.



**Figure 5.** Analysis of Pb in Si wafer using the Agilent 8900 ICP-QQQ in single nanoparticle mode with a 0.1 ms dwell time. Left: One laser shot. Right: 10 laser shots.

## Conclusion

The study has shown that the newly developed LA-GED-MSAG-ICP-MS system overcomes the limitations of conventional LA-ICP-MS technique for the analysis of impurities in semiconductor wafers.

The LA-GED-MSAG-ICP-MS system allows a 12" wafer to be analyzed without the size limitations of a conventional laser ablation cell. Ablated material generated by the laser was collected by the aspiration tube and drawn through the GED before being passed to the ICP-MS. The dual syringe MSAG was used to inject variable volumes of a 1% HNO<sub>3</sub> blank and a standard solution via two syringe pumps to enable a standard addition calibration to be generated for the solid sample ablation. The MSAG syringes gave a consistent total flow of 3 µL/min so that practically 100% of the solution was vaporized and transported to the plasma of the Agilent 8900 ICP-QQQ. This automated method allowed the quantitation of multiple elements by the method of standard addition while ablating the wafer samples.

A fully automated model of LA-GED-MSAG-ICP-MS equipped with two FOUP load ports, a wafer transfer robot, and aligner would enable the unattended analysis of wafers. The method can be considered a supplement to VPD-ICP-MS analysis of Si wafers, as well as offering a solution for the impurity analysis of wafers that are not suited to VPD, such as SiC and GaN wafers. Furthermore, LA sampling can provide spatially resolved data, enabling measurement of discrete features such as particulate contaminants on the wafer surface and depth profiling of various films on wafers.

## References

1. Ichinose, T., Kawabata, K., Sakai, K. Automated Surface Analysis of Metal Contaminants in Silicon Wafers by Online VPD-ICP-MS/MS, Agilent publication, [5994-6135EN](#)
2. Halicz, L., Günther, D. Quantitative analysis of silicates using LA-ICP-MS with liquid calibration, *J. Anal. At. Spectrom.*, **2004**, 19, 1539–1545
3. Suzuki, K., Nishiguchi, K., Kawabata, K., Yamanaka, M. Analysis of Metallic Impurities in Specialty Semiconductor Gases Using Gas Exchange Device (GED)-ICP-MS, Agilent publication, [5994-5321EN](#)

[www.agilent.com/chem](http://www.agilent.com/chem)

DE32495737

This information is subject to change without notice.

© Agilent Technologies, Inc. 2023  
Published in the USA, October 5, 2023  
5994-6670EN