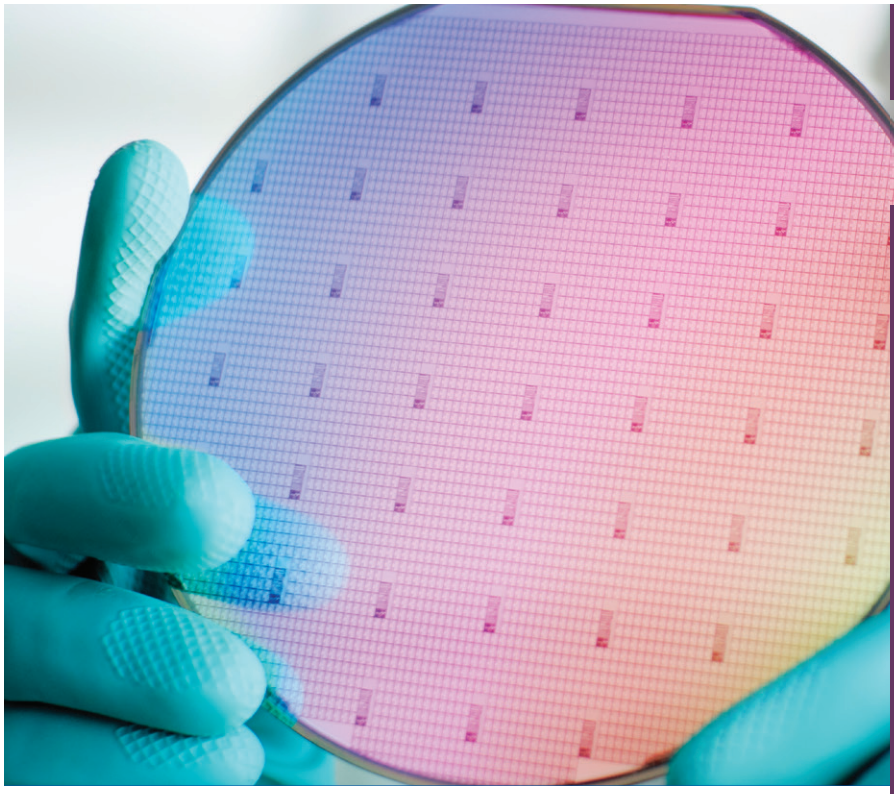

APPLICATION NOTE

ICP - Mass Spectrometry

Authors:

Mina Ichikawa

Yoko Kishi

Tatsu Ichinose

Katsu Kawabata

IAS Inc.
Hino, Tokyo, Japan

Analysis of Metallic Impurities in Si Wafers Using Fully Automated VPD-ICP-MS

Introduction

Silicon (Si) wafers, also known as "silicon slices," are very thin slices of Si material that act as excellent semiconductors and are widely used in modern electronics and advanced electronic components. Silicon is the most used semiconductor and is a critical element for producing circuits found in everyday electronics, such as computers and smartphones, as well as energy conversion applications, such as highly efficient solar cells. As more industries utilize semiconductor devices and Si wafers in electronic products and services, there is an increasing demand for Si wafers with minimal impurities due to ever-growing scale of component integration on a chip. Since Si wafer production involves many microfabrication steps, an essential component of the quality control (QC) process is to have a reliable technique that can identify metallic impurities that could have been introduced during production.

The standard approach is to check each manufacturing step with a control wafer and analyze the Si wafer's surface for impurities. Total reflection x-ray fluorescence (TRXF) has been commonly used as an inline analytical tool to analyze metallic impurities on the Si wafer surface because the technique is non-destructive. While the method is ideal for analyzing the film's surface, impurities inside the film cannot be analyzed. Moreover, the detection limit of TRXF is around E10-E12 atoms/cm^2, which is too far from the current requirements, and some lighter elements, such as Li, Na, Mg, and Al, are difficult or impossible to analyze. To improve the detection capability of the analysis, vapor phase decomposition (VPD) was developed as a pre-concentration technique for TRXF.

PerkinElmer®
For the Better

The VPD technique is a destructive technique that utilizes the reaction chemistry of HF with Si and films deposited on an Si substrate. HF reacts with the films, such as oxide and nitride, but does not react with the Si wafer, so metallic impurities in the films remain on an Si substrate after decomposition of the films. Then, a scan nozzle that holds a scan solution scans the entire surface of the Si substrate collecting metallic impurities, and the scanned solution is dried in a small spot for TRXF analysis. As a result, the detection limits become E8-E10 atoms/cm^2, which are still higher than the requirement. In addition, the dried surface of the nitride film is not smooth, and this causes poor x-ray reflection.

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most sensitive techniques for elemental analysis. It has been used in the semiconductor industry to analyze the sub-ppt levels of metallic impurities in chemicals used for cleaning, etching, drying, as well as in the analysis of Si wafers after the VPD process. The scanned solution can be directly analyzed without drying, and E5-E7 atoms/cm^2 of detection limit can be achieved. Since the Si wafer's surface roughness is not as crucial for ICP-MS analysis as TRXF, ICP-MS technology can be applied to more applications, including bulk Si, metal film, pattern wafer, and noble metals.

This application note will describe the instrument setup, instrument parameters, and analytical steps taken to identify metallic impurities in the silicon wafer production process. The results presented are part of a collaboration between PerkinElmer Inc. and IAS Inc. to create a fully automated solution for quality control and assurance to screen and identify metallic impurities during the Si wafer production process used in semiconductor fabrication (FAB) plants for 24/7 operation.

Experimental

Samples and Sample Preparation

In this application work, all chemicals and solutions were purchased from commercially available suppliers unless specified. For the VPD process, a 50% purity, semiconductor-grade HF (Daikin Industries Ltd., Osaka, Japan) was used. For the preparation of the scan solution, TAMAPURE-AA-100 (Tama Chemicals Co. Ltd., Kanagawa, Japan), HF, H_2O_2, HNO_3, and HCl were used. For a normal scan solution, a 3% HF and 4% H_2O_2 solution as well as an aqua regia (HNO_3/HCl, 1:3 ratio) solution were used for the analysis of chemically resistant noble metals.

A 10 ppb stock standard solution for ICP-MS calibration was prepared in 5% HNO_3 from a 10 ppm multi-element standard solution (XSTC-622B, SPEX CertiPrep, Metuchen, New Jersey, USA). A 10 ppb stock ISTD solution was prepared in 5% HNO_3 from a 1000 ppm single Be and In standard solution (SPEX CertiPrep). Si wafer samples (300 mm) analyzed in this application note were analyzed in a front opening shipping box (FOSB).

Instrumentation Setup

The instrumentation utilized in this application was accomplished by coupling the Expert_PS™ fully automated VPD device (IAS Inc., Hino, Tokyo, Japan) with two 12-foot front opening unified pod (FOUP) load ports to PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS platform. A schematic diagram of the coupled VPD-ICP-MS is shown in Figure 1. Supporting information for the NexION 5000 ICP-MS is described in detail in its product note[1].

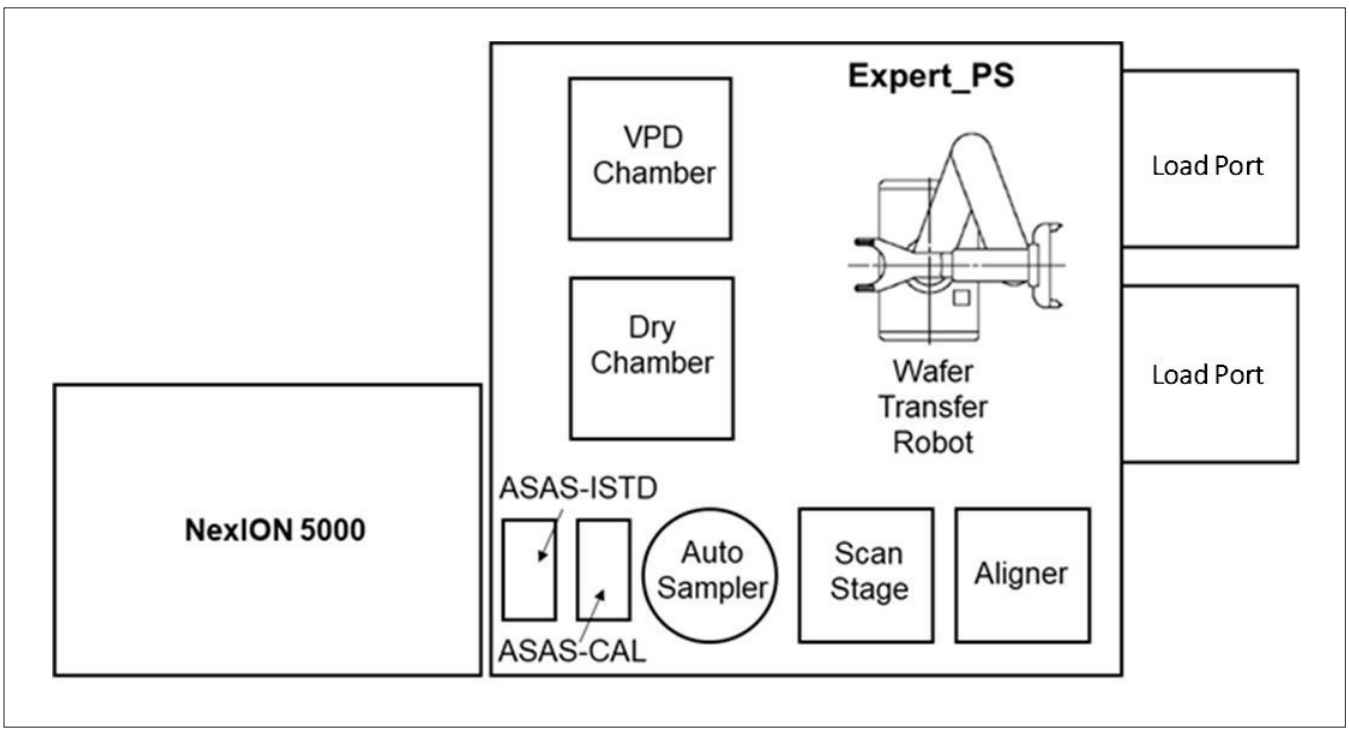

Figure 1. Schematic diagram of the VPD-ICP-MS system.

The Expert_PS VPD system was designed to be compatible with SEMI Equipment Communication Standards (SECS), Generic Equipment Model for Communication and Control of Manufacturing Equipment (GEM300), and Automatic Material Handling System (AMHS) in a semiconductor fabrication plant by communicating with an overhead hoist transport (OHT) using the semiconductor industry-standard protocol SEMI E84.

A FOUP is carried by OHT and loaded on one of the load ports of Expert_PS, and the FOUP ID is read, followed by clamping and docking, and wafer slots are mapped while the FOUP door is opened. The mapping information and FOUP ID are sent to a CIM-HOST, verifying the slot mapping information and assigning the recipe number for each wafer. The CIM-HOST sends back the data to Expert_PS, then the first wafer is taken out from FOUP, after which VPD, scanning, and ICP-MS are performed automatically. After completing ICP-MS analysis, the concentration of pg/mL (ppt) elements is converted into atoms/cm^2 according to the scanned area and sent to the CIM-HOST. The FOUP is automatically taken away by OHT after completing the analysis of all wafers.

There are eight major standard components in the Expert_PS system: load ports, wafer transfer robot (WTR), aligner, VPD chamber, scan stage, autosampler, dry chamber, and automated standard addition system (ASAS). Several optional components include bulk etching module, balance chamber, edge scan, aqua regia scan solution for noble metal analysis, and wafer flip. A wafer is taken out from a FOUP by WTR and aligned and centered by the aligner, adjusting the notch position. The wafer is then transferred to the VPD chamber, in which HF vapor generated by a PFA nebulizer is introduced, and films are etched. Metallic impurities in the films remain as residue on the Si substrate.

The wafer is then transferred to the scan stage. The dual scan nozzle holds a scan solution in contact with the Si substrate's surface and scans an appropriate area to recover metallic impurities on the Si substrate. The scanned solution is collected in one of the vials of the autosampler and analyzed by ICP-MS automatically.

Si's concentration in the scanned solution is around 10 µg/mL (ppm) for a bare wafer, but it can be much higher for some films. If the Si concentration is too high, the sensitivity of ICP-MS might be affected, and deposition of SiO_2 at the tip of the ICP-MS cones occurs. To minimize the deposition at the cones, controlling the temperature of the cone tip is very critical. The NexION 5000 ICP-MS uses Pt cones with a Ni-base that keeps the temperature high to minimize deposition at the cones. The unique hyper-skimmer cone minimizes Na's and K's contamination from cones even under hot plasma conditions. A wafer can be transferred to the dry chamber after the VPD and before the scanning (the pre-dry function) to remove the scan solution's Si matrix. The dry chamber is also used for eliminating any acid residue on an Si wafer after the scan.

Most films can be etched by HF vapor, but some films, such as Si epitaxial, poly-silicon, WSi, and Ti, cannot be etched by HF only. The Expert_PS system has the bulk etching option that uses a mixture of HF vapor and ozone gas, which can etch these films and Si substrate. The bulk etching option can be used for a depth profile of metallic impurities in an ion-implanted Si wafer or metal diffusion behavior in Si substrate with high temperature. However, the wafer surface becomes rough and hydrophilic after the bulk etching, and the scan solution tends to come out from the scanning nozzle. The dual scan nozzle and the N_2 wall option significantly improve the scan solution's holding capability, allowing the scanning of hydrophilic glass or sapphire wafer. Since the bevel and edge area of the wafer makes contact with a cassette, there is a higher possibility of cross-contamination. The Expert_PS system has the patented module that enables the scan of the specified area of the bevel and edge.

Typical critical contamination elements are Fe, Cr, Mn, Ni, Cu, Zn, and Ti, which exist commonly in the environment that can be recovered using a normal scan solution, i.e., a mixture of HF and H_2O_2. However, various new elements have been recently used in the manufacturing process, and different chemistry is required to recover these elements from Si substrate. Aqua regia scan solutions effectively recover noble metals, such as Ru, Au, Pt, and Ag, and are diluted ten times before the ICP-MS analysis. Since the aqua regia scan solution is different from the standard scan solution, other optimization parameters and methods must be used.

Expert_PS software communicates with PerkinElmer's Syngistix™ for ICP-MS software, allowing different calibration curves for each matrix using an automated standard addition system (ASAS). Two ASAS can be integrated into Expert_PS: one is used to add an internal standard solution, and the other is for the standard calibration solution. Around 1 µL/min of internal standard solution (ISTD) and 0.5-10 µL/min of the multi-element standard solution are added to a self-aspirated sample solution. Since the sample uptake rates of the self-aspirated PFA nebulizer vary depending on atmospheric pressure and the sample solution's viscosity, the sample uptake rate is measured by two optical sensors of the ASAS, and an appropriate amount of STD solution is added automatically. Expert_PS software has QC functions to check the performance of the VPD-ICP-MS system. If one of the check items is out of limit, predefined actions will take place automatically. If it is not corrected after the third action, an alarm is sent to the CIM-HOST.

Instrumental Conditions

Table 1 shows the operating conditions of Expert_PS. The VPD time and O_3 generator power were optimized for Si bare wafer and different bulk etching depths. A 120 second pre-drying function was used for the bulk etching wafer. A 1000 µL scan solution was aspirated in the dual scan nozzle, and 800 µL was discharged between the outer and inner nozzle to which vacuum was applied. To avoid the loss of the scan solution, the scan speed for the bulk etched wafer was reduced slightly. A gap between the scanning nozzle and the wafer was kept at 0.2 mm, and the patented N_2 wall option was used only for the aqua regia scan solution. The N_2 wall option pushed back the scan solution into the dual scan nozzle and the vacuum applied to the dual scan nozzle which held the scan solution inside the nozzle.

Table 1. Expert_PS System Operating Conditions.

Parameter	Value
Si Wafer Size	300 mm
VPD Time	200 sec (bare wafer) 600 sec (0.1 µm bulk etching) 1800 sec (1 µm bulk etching)
VPD Gas Flow	1000 mL/min (N_2) 5000 mL/min (O_2 for bulk etching)
O_3 Generator Power	30% (0.1 µm bulk etching) 90% (1 µm bulk etching)
Pre-Dry Time	120 sec at 100 °C
Scan Speed	30 mm/sec (bare wafer) 20 mm/sec (bulk etched wafer)
Scan Solution Volume	1000 µL
Edge Exclusion	5 mm

Table 2 shows the instrument conditions of the NexION 5000 ICP-MS. Only one hot plasma condition was used to have a better decomposition of the Si matrix in the plasma, and NH_3 and O_2 reaction gas were used to overcome interferences.

Table 2. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Nebulizer	C-Flow S (Savillex, MN, USA)
Sample Uptake	105 µL/min measured by ASAS II
Nebulizer Gas Flow	1.0 L/min
Torch	Demountable 2 mm ID Pt injector
RF Power	1500 W Hot Plasma
Measuring Time/Isotope	1 sec
Number of Replicates	3
Cell Modes	Standard and Reaction
Cell Gases	NH_3 and O_2

Results and Discussion

Figure 2 represents the schematic sample flow diagram from the autosampler in the Expert_PS to the PFA nebulizer of the NexION 5000 ICP-MS. The normal scan solution was self-aspirated from the autosampler's rinse port, and the ASAS flow sensors measured the sample uptake rate. The ASAS-CAL syringe pump added an appropriate stock standard solution to make the calibration curve at 0, 0.25, and 1 ppb and followed by a 0.5 ppb QC solution. ASAS-ISTD also added the ISTD solution at 1% of the sample uptake rate. Before analyzing the first wafer in the FOSB, a blank scan solution was taken by the scanning nozzle and analyzed by ICP-MS to ensure that the scanning nozzle and ICP-MS were both clean. The QC solution was analyzed every 10 wafer samples.

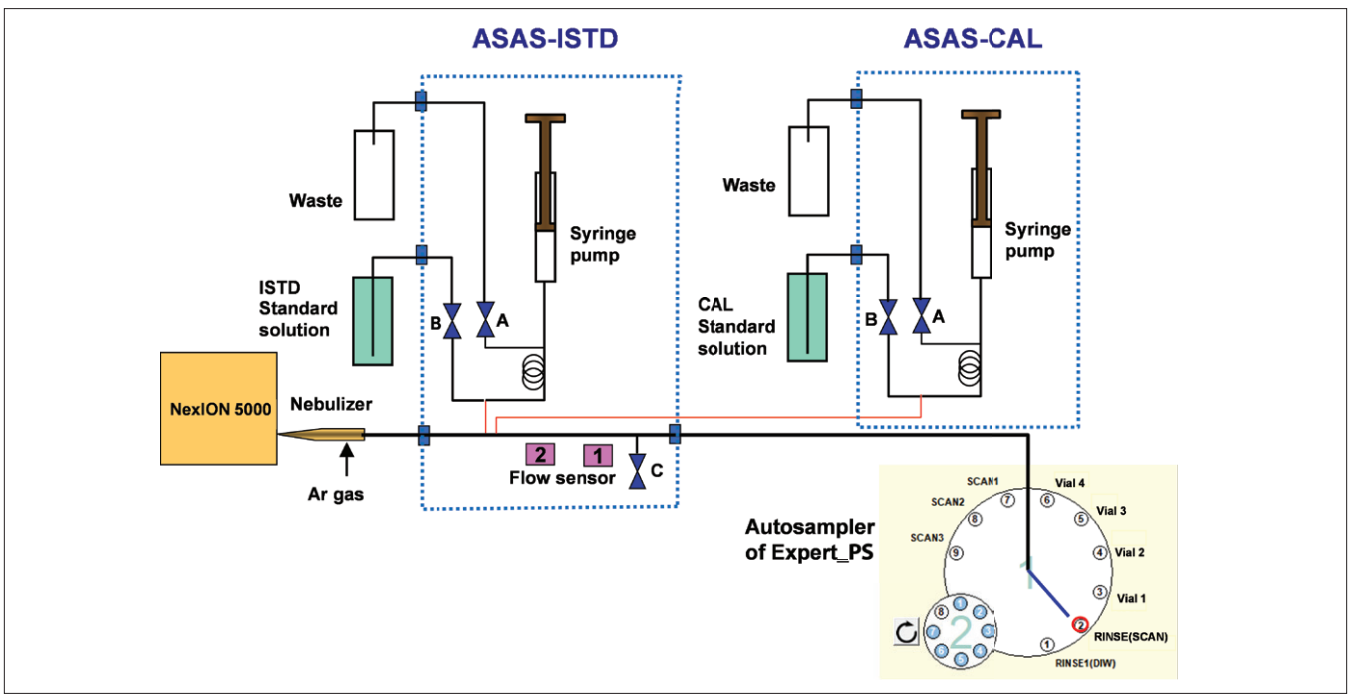

Figure 2. Schematic sample flow diagram of VPD-ICP-MS (NexION 5000 ICP-MS and Expert_PS VPD system).

Table 3 shows the results from the Si bare wafer as well as a 1 µm bulk etched Si wafer, and Figure 3 shows the comparison photo of the wafer surface. The surface became rough, dull, and hydrophilic after the bulk etching, while the Si bare wafer remained shiny and hydrophobic. The concentration of impurities on the Si bare wafer surface were calculated as atoms/cm^2 based on the actual scan area. The bulk etched Si wafer depth was calculated by the weight loss of the Si wafer before and after the bulk etching. The concentration of the impurities in bulk-etched Si wafer were calculated in atoms/cm^3.

Table 3. Results of Si Wafer Analysis.

Analyte	Mode	Q1/Q3	Cell Gas Flow (mL/min)	RPq	Bare Wafer		1 µm Bulk Etching	
					Found (ppt)	Found (atoms/cm2)	Found (ppt)	Found (atoms/cm3)
^{7}Li	STD	7/7	0	0.25	< 0.12	< 1.6E + 07	< 0.12	< 1.6E + 10
^{23}Na	STD	23/23	0	0.25	1.2	4.8E + 07	2.7	1.1E + 11
^{24}Mg	STD	24/24	0	0.25	0.14	5.3E + 06	6.0	2.3E + 11
^{27}Al	DRC (NH_3)	27/27	0.6	0.45	1.1	3.7E + 07	3.1	1.1E + 11
^{39}K	DRC (NH_3)	39/39	0.6	0.45	1.9	4.4E + 07	1.1	2.6E + 10
^{40}Ca	DRC (NH_3)	40/40	1.0	0.45	1.2	2.7E + 07	18	4.1E + 11
^{48}Ti	DRC (NH_3)	48/131	0.6	0.25	< 0.2	< 3.8E + 06	2.1	4.0E + 10
^{51}V	DRC (NH_3)	51/51	0.3	0.45	<0.046	8.2E + 05	0.4	7.2E + 09
^{52}Cr	DRC (NH_3)	52/52	0.6	0.45	1.6	2.8E + 07	2.0	3.5E + 10
^{55}Mn	DRC (NH_3)	55/55	0.6	0.45	0.13	2.2E + 06	0.5	8.3E + 09
^{56}Fe	DRC (NH_3)	56/56	0.6	0.45	1.9	3.1E + 07	2.2	3.6E + 10
^{59}Co	DRC (NH_3)	59/59	0.3	0.45	0.10	1.6E + 06	< 0.088	< 1.4E + 09
^{60}Ni	DRC (NH_3)	60/60	0.3	0.45	0.7	1.1E + 07	2.4	3.7E + 10
^{63}Cu	DRC (NH_3)	63/63	0.3	0.45	1.1	1.6E + 07	1.3	1.8E + 10
^{66}Zn	DRC (NH_3)	66/66	0.3	0.45	0.69	9.6 + 06	< 0.52	< 7.3E + 10
^{69}Ga	DRC (NH_3)	69/69	0.6	0.45	< 0.031	< 4.1E+05	< 0.031	< 4.1E + 08
^{74}Ge	DRC (NH_3)	74/90	0.3	0.45	0.27	3.4E + 06	3.2	4.0E + 10
^{75}As	DRC (O_2)	75/91	1.1	0.45	< 0.64	< 7.8E + 06	8.1	9.9E + 10
^{88}Sr	DRC (NH_3)	88/88	0.6	0.45	< 0.025	< 2.6E + 05	0.15	1.6E + 09
^{90}Zr	STD	90/90	0	0.25	< 0.1	< 1.0E + 06	< 0.1	< 1.0E + 09
^{98}Mo	DRC (NH_3)	98/98	0.6	0.45	0.33	3.1E + 06	< 0.31	3.0E + 09
^{107}Ag	STD	107/107	0	0.25	< 0.19	< 1.6E + 06	3.9	3.3E + 10
^{111}Cd	STD	111/111	0	0.25	< 0.18	< 1.5E + 06	< 0.18	< 1.5E + 09
^{118}Sn	STD	118/118	0	0.25	< 0.28	< 1.5E + 06	12	9.2E + 10
^{138}Ba	STD	138/138	0	0.25	< 0.048	< 3.2E + 05	< 0.048	< 3.2E + 08
^{184}W	STD	184/184	0	0.25	< 0.15	< 7.4E + 05	< 0.15	< 7.4E + 08
^{208}Pb	DRC (NH_3)	208/208	0.6	0.45	< 0.13	< 5.7E + 05	< 0.13	< 5.7E + 08

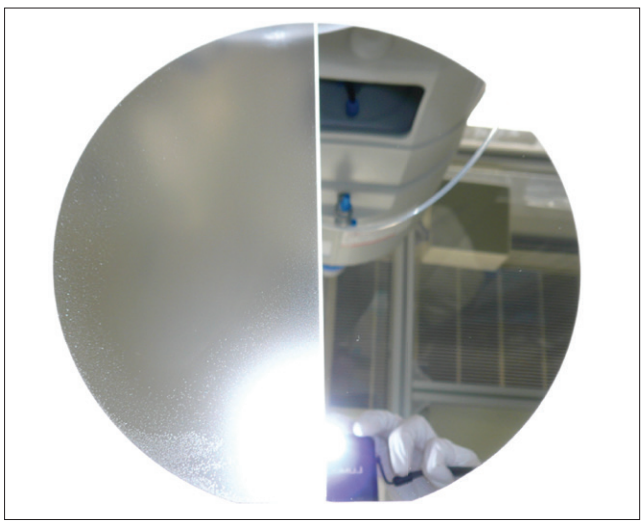

Figure 3. Photos of Si wafer surface - Left: after the Si bulk etching; Right: Si bare.

Figure 4 shows a magnified image of the edge scan. A 300 µL of normal scan solution was discharged between the inner nozzle of the dual scan nozzle and the edge plate, to contact the Si wafer's bevel and edge.

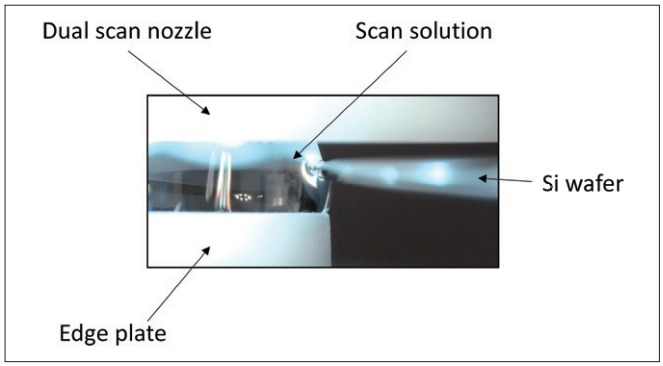

Figure 4. Magnified photos of the edge scan.

Figure 5 represents the depth profile of ^{11}B implanted Si wafer. A 0.1 µm bulk etching was repeated 20 times. The target ^{11}B implanted depth was at 1 µm, and the depth profile showed good agreement. Some impurities, such as Al and Fe, were detected at a shallower level.

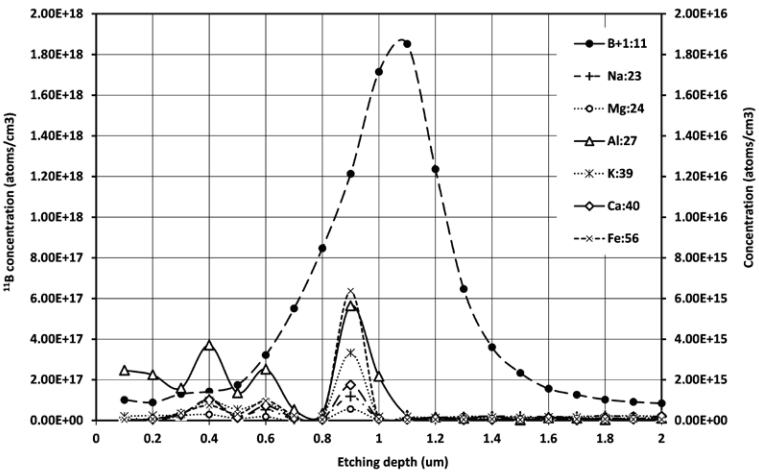

Figure 5. Depth profile of ^{11}B implanted Si wafer.

Table 4 shows the recovery of noble metals on the Si wafer. A spiked wafer was prepared by dropping a 1000 µL of 1 ppb multi-element standard solution on a Si bare wafer. Only the scan was repeated three times using the concentrated aqua regia scan solution after the VPD. The scanned aqua regia solution was automatically diluted with DIW 10 times before ICP-MS analysis. As can be seen, some elements showed lower recoveries with the normal HF + H_2O_2 scan solution, whereas the aqua regia scan solution improved analyte recoveries. Three modes of operation were used for the NexION 5000 ICP-MS to overcome interferences. Reaction mode with NH_3 reaction gas and Focusing ion guide mode (IGM) effectively remove many interfering ions. Mass Shift mode with Extraction ion guide mode was used to analyze some elements such as Ti, Ge, and As. ^{48}Ti was analyzed on mass 131 as $^{48}Ti(^{14}N^{1}H_3)_4{}^{14}N^{1}H$ using NH_3 as a reaction gas, and ^{75}As was analyzed on mass 91 as $^{75}As^{16}O$ using O_2 as a reaction gas to avoid the interference of SiO and ArOF, respectively. ^{74}Ge didn't have any particular interferences on mass 74, but $^{74}Ge^{14}N^{1}H_2$ clustering with NH_3 as a reaction gas on mass 90 gave good sensitivity and lower background equivalent concentrations (BECs) than alternative approaches.

Conclusion

The results presented in this application work, performed in collaboration between PerkinElmer Inc. and IAS Inc., demonstrate that the Expert_PS VPD system can be coupled with the NexION 5000 Multi-Quadrupole ICP-MS to provide a fully automated solution for the analysis of metallic impurities in silicon wafers. This is due to the ICP-MS' sensitivity and its ability to remove spectral inferences when performing trace analysis in combination with a platform that eliminates manual operation and chemical exposure to operators to prevent Si wafer contamination.

References

1. "NexION 5000 Multi-Quadrupole ICP-MS" PerkinElmer Product Note, 2020.

Table 4. Recovery (%) of Elements from Si Wafer with Different Scan Solutions.

Scan Solution	Element						
	Au	Ir	Pt	Rh	Ru	Pd	Ag
3% HF + 4% H_2O_2	7	28	20	25	26	14	9
Aqua Regia	99	99	89	91	92	98	99

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

224086 PKI