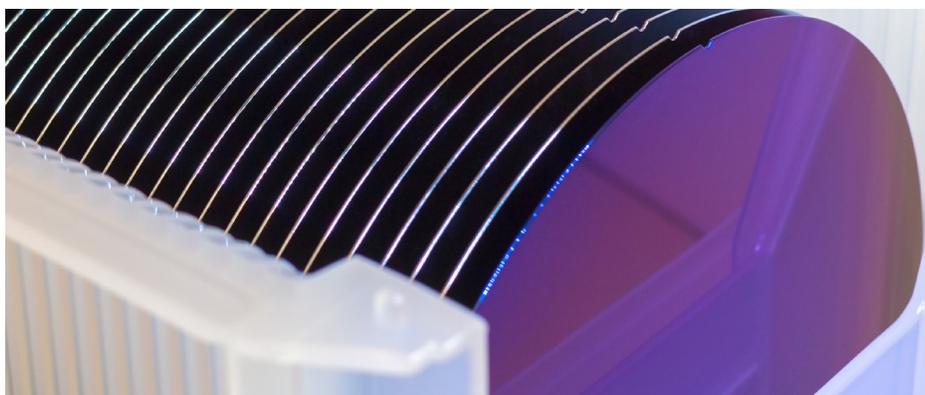


Automated Surface Analysis of Metal Contaminants in Silicon Wafers by Online VPD-ICP-MS/MS

Agilent 8900 ICP-QQQ integrated with IAS Expert PS VPD provides the sensitivity and robustness required for 24/7 contamination control of wafers



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Introduction

Semiconductor microchips or integrated circuits (ICs) are used in thousands of products that impact practically every aspect of modern life. During the manufacture of these ICs, semiconductor fabrication plants (FABs) require strict control of all sources of contamination to minimize yield losses and ensure that the finished chip delivers the required reliability and performance (1). Most ICs are built on a substrate or “wafer” of silicon, which is made by purifying quartzite (sand) to produce bulk, polycrystalline silicon. Polysilicon is further processed to create a pure, monocrystalline silicon ingot from which the wafers are sliced.

The main contaminant elements in quartzite are iron (Fe), aluminum (Al), calcium (Ca), and titanium (Ti), while other elements may be introduced during the carbothermic processes used to convert quartzite into 98% pure silicon (Si). Gas phase purification and chemical vapor deposition remove most of the impurities, leaving silicon of around 8 nines (8N) purity, suitable for making the wafers used for IC fabrication. 8N is 99.999999% purity, so total contaminant levels of less than 10 ng/g (ppb) in the solid Si. Processes such as slicing and polishing, used during preparation of the blank wafers, can introduce trace element contamination, for example from the chemical mechanical planarization or polishing (CMP) slurries. Metallic contamination may also be introduced during subsequent “front-end” processes such as cleaning, etching, oxide growth, and ion implantation.

The elements of most concern in IC fabrication are the transition metals and alkaline elements, but the distribution of these elements in the Si wafer is not necessarily uniform. Fe can diffuse through the bulk Si substrate into the surface oxide layer, while Ti impurity levels may vary due to segregation during melting and cooling of the monocrystalline Si ingot. To ensure that metal contaminants are not present at levels that could adversely affect the IC device, the concentration of trace metals in the wafer must be monitored using a suitable surface analysis technique. The bare Si layer on the surface of the wafer quickly oxidizes to SiO₂ when exposed to atmospheric oxygen (O₂) and water. This naturally oxidized layer is less than 2 nm thick (2). If the IC design requires an insulating film, a much thicker oxide layer is formed on the wafer surface by heating the wafer to 900–1200 °C in the presence of O₂ or water vapor. This thermally oxidized layer may be up to 100 nm (0.1 μm) thick.

For both native and thermally oxidized SiO₂, the trace metals in the oxide layer can be measured at extremely low concentrations using vapor phase decomposition (VPD) coupled with ICP-MS. VPD-ICP-MS can also be used to analyze metallic contaminants in other wafer surface layers and films such as silicon nitride (SiN). VPD is a surface metal extraction (SME) technique that uses hydrogen fluoride (HF) vapor to decompose the surface SiO₂ layer of the wafer ($\text{SiO}_2 + 6 \text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O}$). The contaminant metals released from the SiO₂ layer, together with the H₂SiF₆ remaining on the wafer surface, are collected by scanning a droplet of a recovery solution across the wafer surface. The recovery solution is usually a mix of dilute HF and hydrogen peroxide (H₂O₂), but sometimes an alternative solution such as hydrochloric acid/peroxide mix (HCl/H₂O₂) is used. After collecting the dissolved metallic contaminants, the droplet is pipetted from the wafer surface and transferred to the ICP-MS for analysis.

Surface metal contamination can also be measured by total reflection X-ray fluorescence (TRXRF), which is a non-destructive technique but has relatively poor detection limits (DLs) of E+10–E+12 atoms/cm². TRXRF DLs can be improved by preconcentrating the metal contaminants into a dried VPD droplet, but VPD-ICP-MS provides much higher sensitivity, especially for lighter mass elements, Li, Na, Mg, and Al. When a high sensitivity triple quadrupole ICP-MS system (ICP-QQQ) such as the Agilent 8900 ICP-QQQ is used, typical VPD-ICP-MS DLs range from E+05 to E+07 atoms/cm² compared to E+08–E+10 atoms/cm² DLs for VPD-TRXRF. VPD-ICP-MS is also more easily automated than VPD-TRXRF, so is better suited to the needs of FABs for online monitoring of ultratrace contaminants in Si wafers.

Many large semiconductor FABs use automated VPD systems integrated with an Agilent ICP-MS for routine production control of trace metal contaminants in Si wafers. Compared to manual systems, automated VPD-ICP-MS is less labor intensive, reduces the potential for contamination, and generates higher-quality data. Agilent ICP-MS instruments are compatible with all leading automated (and manual) VPD systems, with performance proven in multiple installations in leading FABs worldwide.

As shown schematically in Figure 1, the VPD-ICP-MS process involves three steps:

1. The Si wafer is placed in a VPD chamber and exposed to HF vapor, which decomposes the native oxide or thermally oxidized SiO₂ surface layer, leaving the metallic contaminants deposited on the wafer surface.
2. A scan droplet (for example 250 to 1000 μL of 3% HF/4% H₂O₂) is placed on the wafer and the droplet is “scanned” in a carefully controlled pattern across the wafer surface. As the scan droplet moves across the wafer, it collects the contaminant metals freed from the SiO₂ layer in Step 1.
3. The scan droplet is transferred from the wafer surface to an ICP-MS or ICP-QQQ for analysis.

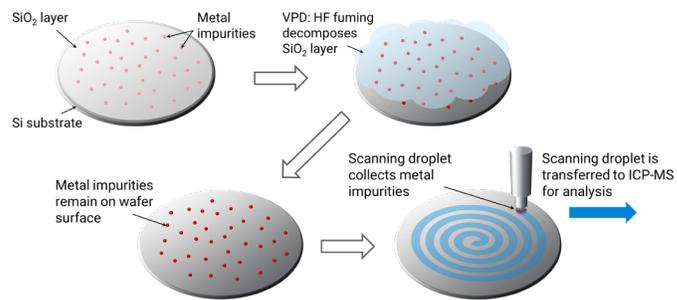


Figure 1. Outline of the VPD-ICP-MS process.

In this study, a fully automated VPD-ICP-MS system comprising the IAS Expert PS (IAS Inc., Hino, Tokyo, Japan) integrated with an Agilent 8900 ICP-QQQ was used. The automated VPD-ICP-MS/MS method was evaluated by deliberately contaminating the Si wafer surface with known amounts of trace elements and measuring the recoveries in the VPD scan droplet.

The Expert PS automated VPD-ICP-MS system (3, 4) is compatible with the Automated Standard Addition System (ASAS) from IAS Inc. (5, 6). In this work, one ASAS (ASAS-Cal) was used to prepare external calibration standards from a stock solution and to automate the spike recovery tests. The ASAS can also automatically add online spikes to generate a method of standard additions (MSA) calibration curve. The internal standard (ISTD) solution was automatically introduced to the ICP-MS using a second ASAS (ASAS-ISTD). In addition to simplifying the analysis, the use of an automated sample introduction system decreases manual sample handling, minimizes errors, and reduces the potential for sample contamination. A schematic of the ASAS/VPD-ICP-MS system is shown in Figure 2.

Experimental

VPD HF fuming and scan droplet solutions

The solutions for the respective Expert PS chemical ports were prepared in a clean room. The solution used to generate HF vapor was prepared from wet-etching semiconductor-grade HF (50% aqueous solution from Daikin Industries Ltd., Osaka, Japan).

Two solutions were prepared from TAMAPURE-AA-100 reagents (Tama Chemicals Co. Ltd., Kanagawa, Japan) for the scan droplets used to collect the dissolved metals. A solution of 3% HF and 4% H₂O₂ was used to recover most metals, while a second solution of aqua regia (one-part HNO₃ to three parts HCl) was used to recover the precious metals. The aqua regia scan solution was diluted 10-fold after scanning and before being introduced into the ICP-MS.

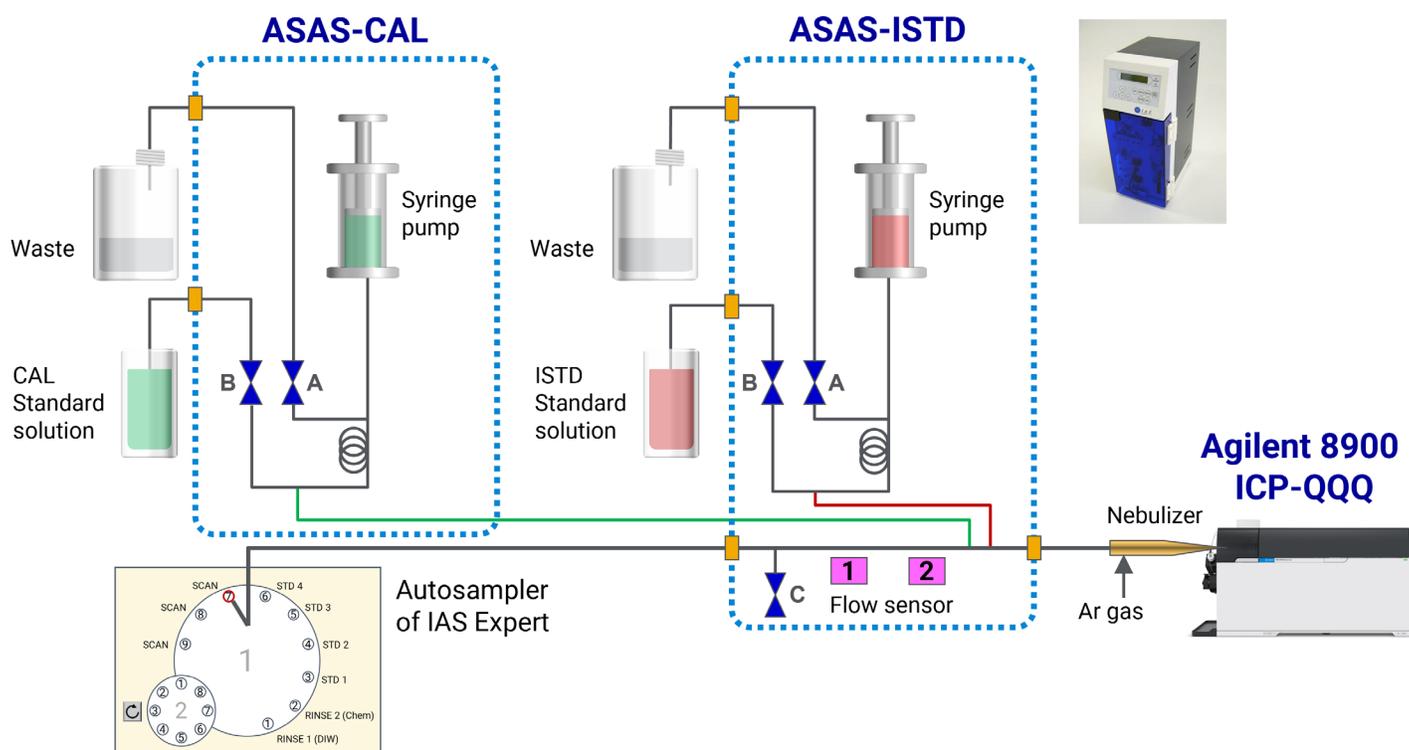


Figure 2. Schematic of the ASAS and autosampler, which are integral parts of the automated VPD-ICP-MS system. Schematic modified from image supplied by IAS Inc.

Calibration standards for the ASAS-Cal system

A 10 ng/mL (ppb) mixed multi-element standard solution was spiked into a high purity 3% HF/4% H₂O₂ solution to create the calibration standards for external calibration. The working standard solution was prepared by diluting a 10 µg/mL (ppm) mixed multi-element standard (SPEX CertiPrep, Metuchen, NJ, US) with 5% HNO₃. The 10 ppb working standard solution was placed in a clean sample bottle and connected to the standard line of the ASAS-Cal system. All calibration solutions required for the analysis were automatically prepared by the ASAS in the same matrix composition as the scan solution.

For the spike recovery test, a 5 ppb multi-element standard solution was prepared. A 1000 µL volume of the spike solution was dropped onto the surface Si wafer surface and allowed to dry. The Si wafer surface was scanned with the scan solution to collect the contaminant elements and the scan droplet was then introduced into the ICP-MS.

Internal standards for the ASAS-ISTD system

The second ASAS was used to introduce the ISTD solution containing 10 ppb beryllium (Be) and indium (In) in 5% HNO₃, prepared from 1000 ppm single element standards (SPEX CertiPrep). The ISTD solution was mixed online with the sample to give a final ISTD concentration of 100 pg/mL (ppt).

Samples

The 300 mm (12 inch) Si wafer samples analyzed in this study were supplied by a FAB located in Japan and were shipped in a Front Opening Shipping Box (FOSB). Some types of FOSB can be docked directly to the VPD-ICP-MS. Alternatively, a Front Opening Unified Pod (FOUP) that is commonly used in FABs for transporting wafers can be handled by the Expert PS. A FOSB or FOUP can contain up to 25 wafers.

Instrumentation

ICP-MS

An Agilent 8900 ICP-QQQ (#200, Semiconductor configuration) was optically aligned with and coupled to the IAS Expert PS (Figure 3) to create the fully integrated and automated VPD-ICP-MS system. The sample introduction system of the ICP-QQQ comprised a PFA inert kit with C-Flow nebulizer (Saville, Eden Prairie, MN, USA), and the 8900 was fitted with the standard platinum-tipped interface cones.

The 8900 ICP-QQQ has an exceptionally robust plasma to provide the matrix tolerance required for the analysis of thermally oxidized SiO₂, where the Si matrix concentration can be up to 5000 ppm in the scan droplet (depending on the thickness of the oxide layer). The 8900 has the added benefit of extremely high sensitivity and ultralow background (typically <0.1 cps) combined with MS/MS operation, which provides effective removal of spectral overlaps, to deliver lower detection limits and improved accuracy.

In advanced semiconductor applications, the key requirement is to deliver the absolute lowest possible detection limits for each analyte. Laboratories measuring ultratrace levels of contaminant metals often use a multitune method, where several tuning steps are applied sequentially during the measurement of each solution. This approach allows the tuning conditions to be optimized for the removal of different types of interferences, while maintaining sensitivity for each analyte. In this work, several plasma conditions (hot, warm, and cool) and reaction cell gases (O₂ and H₂) were used for the analytes being measured. Advanced, high stability electronics in the plasma RF generator combined with low cell volume and fast cell gas switching times (stabilization time of only a few seconds) mean that multiple tune steps can easily be completed for each analysis, even for small sample volume VPD scan solutions.

Expert PS

The Expert PS VPD-ICP-MS system is designed to be installed in FABs and be integrated with the FAB's computer integrated manufacturing (CIM) host system. The Expert PS is therefore fully compatible with SEMI protocols for automated systems, including the communication with FOUPs via an overhead hoist transport (OHT). In a FAB, the OHT delivers a FOUP containing multiple Si wafers into one of the load ports of Expert PS. Once the FOUP has been identified, the analysis of each wafer in turn by VPD-ICP-MS is fully controlled by commands sent via the CIM-host, and the ICP-MS analysis results are returned to the CIM-host. When all wafers in the FOUP have been analyzed, the OHT automatically removes the FOUP from the load port of the Expert PS.

The basic operating conditions of the Expert PS and 8900 ICP-QQQ are given in Tables 1 and 2, respectively.

Table 1. IAS Expert PS operating parameters.

Parameter	Value
Si Wafer Size (mm)	300
VPD Time (s)	200
VPD Gas Flow (mL/min)	1000
O ₃ Generator	Not used
Pre-dry	Not used*
Scan Speed (mm/sec)	30
Edge Exclusion (mm)	5
Scan Solution 1	3% HF + 4% H ₂ O ₂
Scan Solution 2	Aqua regia
Scan Solution Volume (μL)	1000

* Only used for bulk etching and special films.

Table 2. Agilent 8900 ICP-QQQ operating conditions.

Parameter	Tune Mode 1, Cool Plasma, H ₂ +He	Tune Mode 2, Warm Plasma, H ₂ +He	Tune Mode 3, Hot Plasma, He+O ₂	Tune Mode 4, Hot Plasma, O ₂
RF Power (W)	600	1200	1500	
Sampling Depth (mm)	20			
Nebulizer Gas Flow Rate (L/min)	0.80			
Makeup Gas Flow Rate (L/min)	0.45	0.65	0.50	
Sample Uptake Rate (μL/min)	100 (controlled by ASAS)			
Cell Gas (Flow Rate, mL/min)	He (1.0); H ₂ (3.0)	He (4.0); H ₂ (2.0)	He (2.0); O ₂ (0.2 or 15% of full scale)	O ₂ (0.4 or 25% of full scale)
Integration Time (sec/isotope)	1.0			

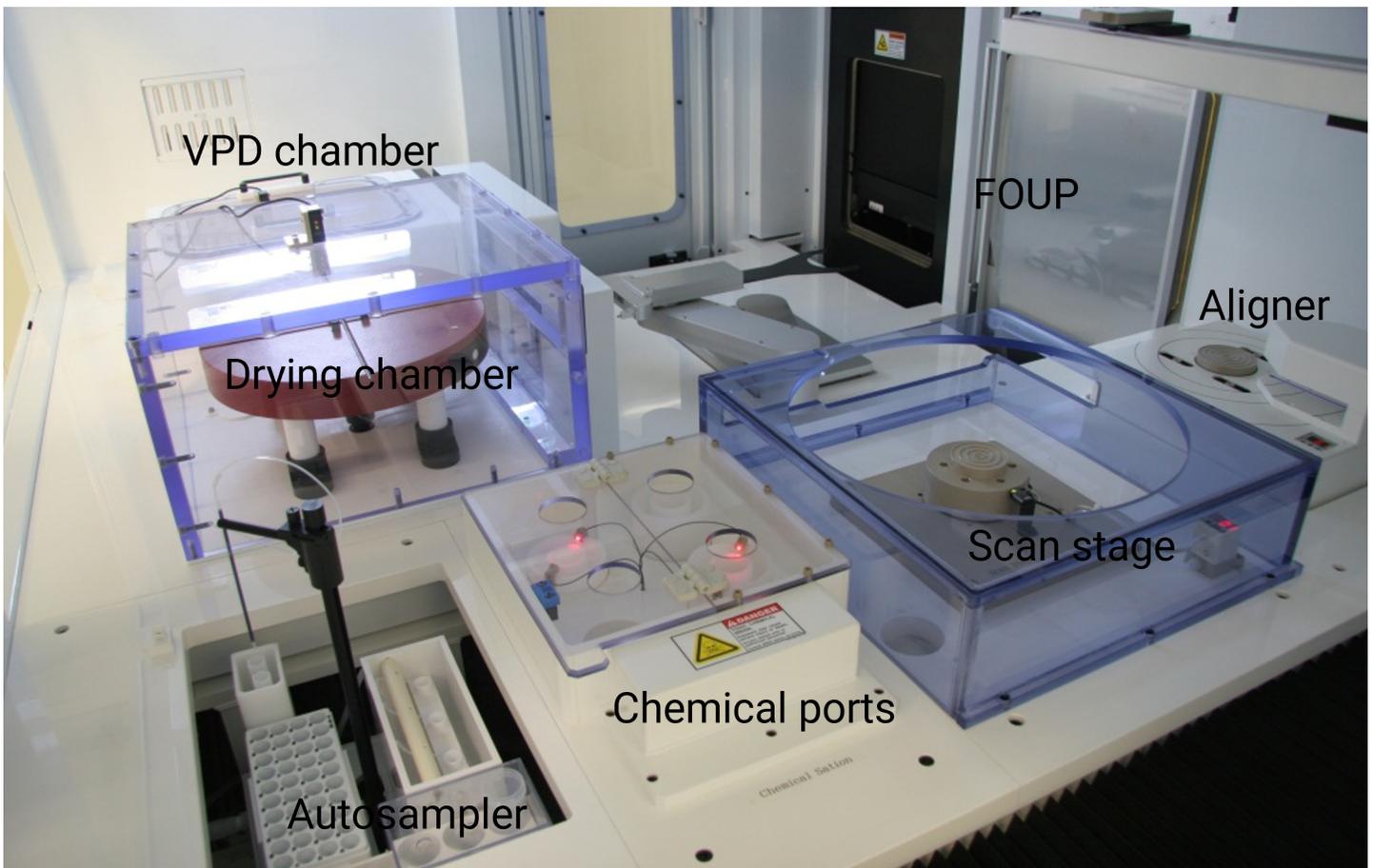


Figure 3. Internal view of the Expert PS. Photo courtesy of IAS Inc.

The fully automated VPD-ICP-MS procedure is controlled using Intelligent VPD-ICP-MS software developed by IAS for the Expert systems. The procedure is described in reference 4, and includes the following actions:

1. The interface software automatically performs calibration and QC checks.
2. The two ASAS systems automatically add both the ISTD solution and ICP-MS calibration standard solution.
3. The scan nozzle and vials used for collecting scan solution are rinsed and washed automatically.
4. The software generates elemental concentration results in atoms/cm², as explained by equation 1.

Equation 1: Calculation of concentration of an element on the Si wafer:

$$\text{Concentration on wafer (atoms/cm}^2\text{)} = \frac{\text{From Expert (Scan volume (mL))} \times \text{From ICP-MS (ICP-MS result (pg/mL))} \times 10^{-12} \times N_A \text{ (atoms/mol)}}{\text{Atomic weight (g/mol)} \times \text{Scanned area (cm}^2\text{)}}$$


N_A = Avogadro constant

For example, 1 ppt (pg/mL) of Fe, 1 mL of scan solution, 300 mm wafer (706 cm²) equates to 1.5 x 10⁷ atoms/cm² (often described within the industry as 1.5 E+07). The calculation is done automatically by the software.

Results and discussion

Detection limit of VPD-ICP-MS

The detection limits shown in Table 3 were calculated from the standard deviation of three replicate measurements of the scan blank solution multiplied by three (3 x SD).

Table 3. VPD-ICP-MS acquisition conditions and detection limits.

Element	Tune Mode	MS/MS Settings		Detection Limit	
		Q1	Q2	pg/mL	Atoms/cm ²
Li	Cool, H ₂ /He	7		0.02	2.3 E+06
Na	Cool, H ₂ /He	23		0.49	1.8 E+07
Mg	Cool, H ₂ /He	24		0.13	4.5 E+06
Al	Cool, H ₂ /He	27		0.94	3.0 E+07
K	Cool, H ₂ /He	39		0.26	5.7 E+06
Ca	Cool, H ₂ /He	40		0.71	1.5 E+07
Ti	Hot, O ₂	48	64	0.23	4.1 E+06
V	Hot, O ₂	51	67	0.07	1.2 E+06
Cr	Cool, H ₂ /He	52		0.10	1.6 E+06
Mn	Cool, H ₂ /He	55		0.01	2.3 E+05
Fe	Cool, H ₂ /He	56		0.57	8.7 E+06
Co	Cool, H ₂ /He	59		0.12	1.7 E+06
Ni	Cool, H ₂ /He	60		0.37	5.4 E+06
Cu	Cool, H ₂ /He	63		0.27	3.6 E+06
Zn	Hot, O ₂	64		0.31	4.1 E+06
Ge	Hot, He/O ₂	74		0.52	6.1 E+06
Sr	Hot He/O ₂	88		0.02	1.7 E+05
Zr	Hot, O ₂	90	106	0.10	8.9 E+05
Nb	Hot, O ₂	93	125	0.02	1.5 E+05
Mo	Hot, He/O ₂	95	127	0.09	7.8 E+05
Sn	Hot, He/O ₂	118		0.71	5.1 E+06
Sb	Hot, He/O ₂	121		0.22	1.5 E+06
Ba	Hot, He/O ₂	138		0.09	5.9 E+05
Hf	Hot, He/O ₂	178	194	0.04	2.1 E+05
Ta	Hot, He/O ₂	181	213	0.02	1.2 E+05
W	Hot, He/O ₂	182	214	0.05	2.2 E+05
Pb	Warm, H ₂ /He	208		0.47	1.9 E+06

Quantitative data and spike recovery ratios

The quantitative analysis results for impurities on the surface of a Si wafer obtained by VPD-ICP-MS/MS are shown in Table 4. The results are reported as pg/mL and atoms/cm².

To evaluate the accuracy of the quantitative method, the spiked Si wafer was analyzed three times using the automated VPD-ICP-MS system. The recovery ratio for each element was calculated using the following equation, based on the three droplet scans:

$$(1st / (1st + 2nd + 3rd)) \times 100$$

As shown in Table 4, all recoveries were within 100 ±5%, apart from Cu, which had 81% recovery. Cu has a strong affinity for the Si wafer, so some of the Cu is retained on the wafer surface, rather than being dissolved into the HF+H₂O₂ scan solution.

Table 4. Quantitative data and spike recoveries for elements analyzed in the HF + H₂O₂ scan solution.

Element	Measured Concentration		Spike Recovery
	pg/mL	Atoms/cm ²	%
Li	<0.02	<2.3 E+06	100
Na	<0.49	<1.8 E+07	100
Mg	1.30	4.6 E+07	98
Al	1.53	4.8 E+07	98
K	<0.26	<5.7 E+06	100
Ca	4.59	9.8 E+07	98
Ti	0.60	1.1 E+07	100
V	<0.07	<1.2 E+06	99
Cr	0.17	2.8 E+06	99
Mn	<0.01	<2.3 E+05	100
Fe	7.22	1.1 E+08	99
Co	<0.12	<1.7 E+06	100
Ni	0.53	7.7E+06	100
Cu	0.43	5.8 E+06	81
Zn	<0.31	<4.1 E+06	100
Ge	<0.52	<6.1 E+06	99
Sr	<0.02	<1.7 E+05	98
Zr	<0.10	<8.9 E+05	100
Nb	<0.02	<1.5 E+05	97
Mo	<0.09	<7.8 E+05	98
Sn	7.41	5.3 E+07	99
Sb	<0.22	<1.5 E+06	99
Ba	0.62	3.8 E+06	98
Hf	<0.04	<2.1 E+05	100
Ta	<0.02	<1.2 E+05	97
W	0.30	1.4 E+06	96
Pb	<0.47	<1.9 E+06	95

The platinum group elements (PGEs), Ag, and Au, have an even stronger affinity for the Si wafer than Cu. For the PGEs, it is therefore recommended to use a separate scan solution of aqua regia (a 3:1 mix of concentrated HCl:HNO₃). The spike recovery results for six precious metals analyzed in the aqua regia scan solution are shown in Table 5. The scan solution was diluted 10-fold after scanning and before analysis by ICP-MS/MS. All recoveries were within 100 ±10%, apart from Pt, which was recovered within ±15%.

Table 5. Spike recovery ratios for precious metals analyzed in the aqua regia scan solution.

	Pd	Ag	Ir	Pt	Au	Ru
Recovery (%)	90	96	95	86	93	90

Conclusion

The automated VPD-ICP-MS system provided accurate analysis of elemental contaminants in Si wafers, minimizing sample handling and thereby reducing the risk of contamination. Integrating the Agilent 8900 ICP-QQQ within the IAS Expert PS ensures detection of contaminants at ultratrace-levels due to the advanced interference removal capabilities and high sensitivity of the ICP-MS/MS method.

Detection limits below 3.0 E+07 atoms/cm² (<1 pg/mL) were achieved for all elements and the spike recovery data demonstrated the accuracy of the method for the determination of ultratrace contaminants in Si wafers.

The IAS Expert PS/Agilent 8900 automated VPD-ICP-MS system has a proven track record of supporting IC manufacturing in the most advanced semicon FABs worldwide. The industry acceptance of the integrated IAS VPD and Agilent ICP-MS/MS system is due to the robustness and reliability of the equipment and the stability and high performance of the instrumentation. The VPD-ICP-MS/MS system can be fully integrated into a FAB's computer integrated manufacturing system enabling unattended operation and contamination control of Si wafers 24 hours a day, 365 days a year.

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