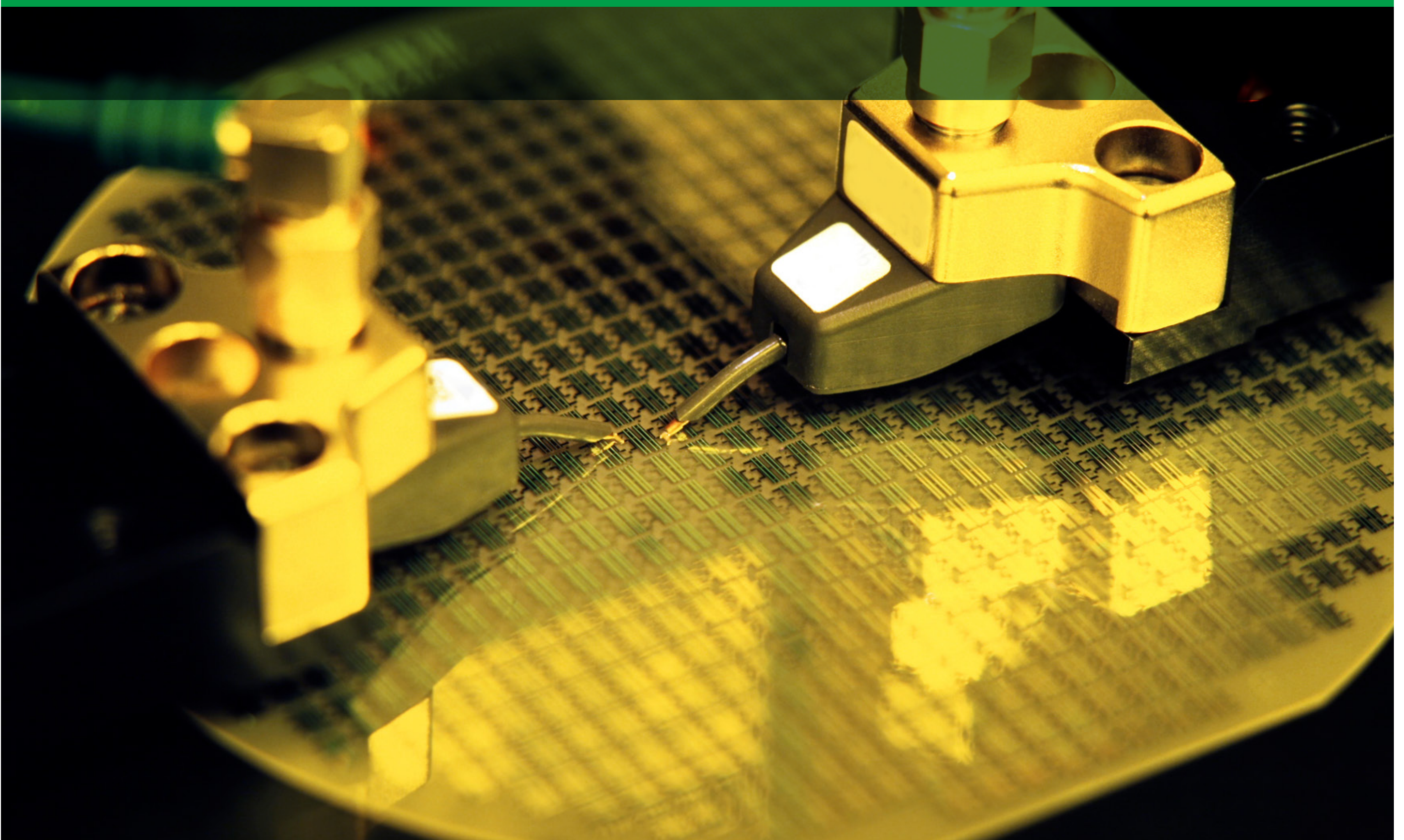
Agilent

Trusted Answers

Agilent Atomic Spectroscopy Solutions for the Semiconductor Industry



Contents

Trace Elements in the Semiconductor Industry 3

Three Decades of ICP-MS Experience Drives Continuous Innovation 6

Agilent ICP-MS Solutions for the Semiconductor Industry 7

Setups for Different Sample Types 8

Automating Analysis of Metal Contaminants in Si Wafers 12

Expanding Capabilities with Accessories and Software 14

Online Monitoring of Metal Contaminants in Process Chemicals 15

Contamination Control 16

Other Agilent Atomic Spectroscopy Solutions for the Semiconductor Industry 24

Trace Elements in the Semiconductor Industry

Today's technological world relies on the integrated circuits (ICs) that are found in devices ranging from manufacturing robots to smart light bulbs, and from mobile telephones to automobiles, aviation and aerospace.

A silicon-based IC device is fabricated from millions of individual transistors (or switches) packed onto a silicon wafer chip. The device is built from patterned layers of oxide, polysilicon, silicon nitride dielectric, and conducting metal interconnects. Layers are connected by "vias" to form a 3D structure that provides the required computing or memory functionality.

During the integrated circuit fabrication process (shown in Figure 1), each conducting or insulating layer is deposited, masked, and etched. This leaves an intricate pattern of features with line widths as small as 10 nanometers (equivalent to about 40 Si atoms). Doped regions are added, depositing or implanting specific atoms to alter the conductivity of the silicon.

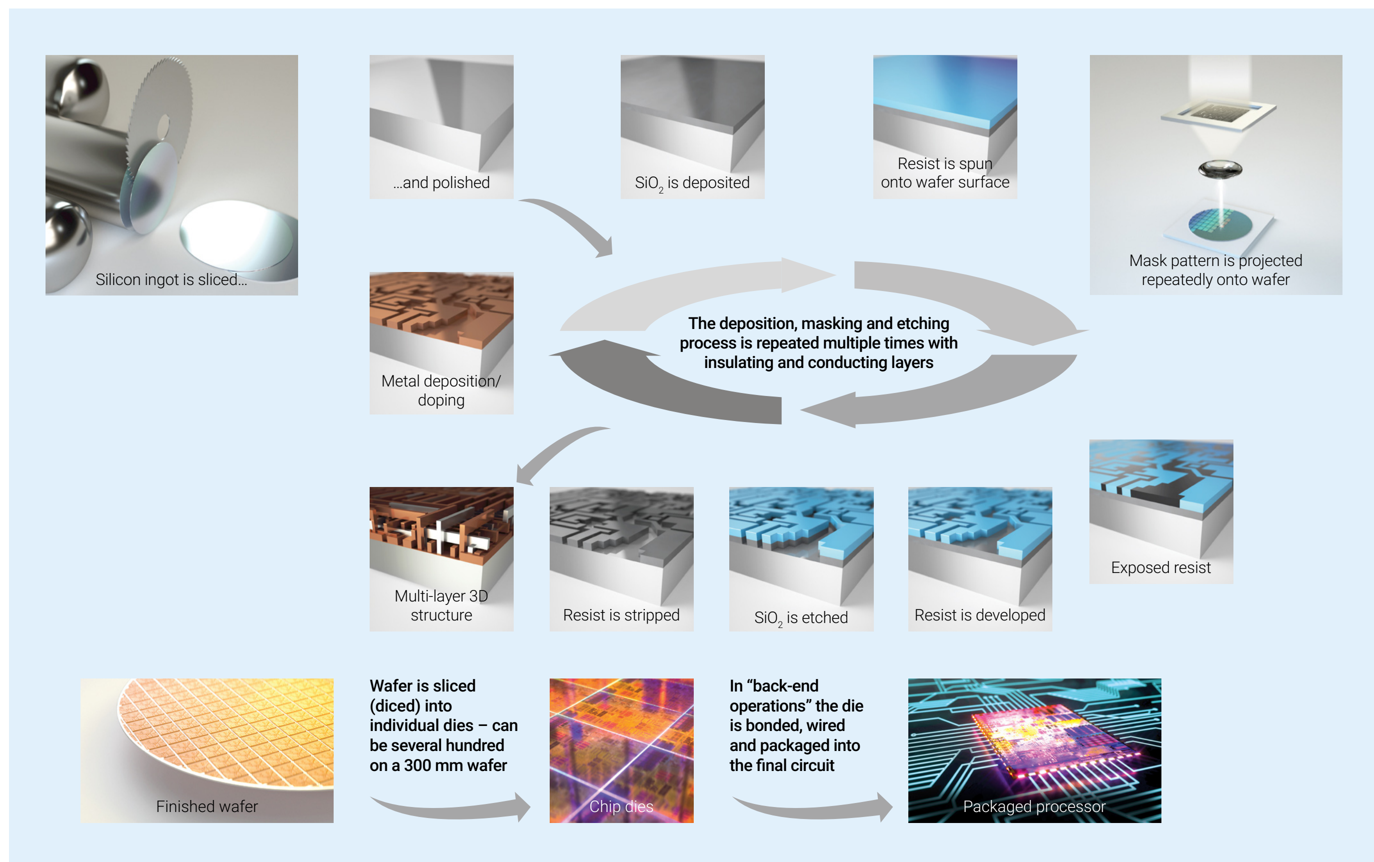


Figure 1. Simplified schematic showing typical steps in silicon wafer fabrication.

SEMI specifications

SEMI is a global semiconductor industry association that publishes standards and specifications for process chemicals and gases, among many other things.
Many semiconductor industry manufacturers are currently working with Grade 3 or 4 chemicals (Tier-B or Tier-C specifications, suitable for geometries between 800 and 90 nm). However, with the development of smaller architectures, there is pressure to move to Tier-D and Tier-E chemical specifications. Tier-E requires DLs below 0.1 ppt and accurate spike recovery of target elements at 0.5 ppt. Accurate analysis at these lower levels requires the higher performance of ICP-QQQ.

The current "10 nanometer" geometry contains features approximately 1000 times smaller than circuits manufactured in the 1970s. This reduced scale and increased density has required a parallel improvement in the control of contamination. The resultant need for higher-purity chemicals has led to ever-higher demands on the performance of the analytical instruments used to detect metallic impurities, a trend that is likely to continue.

Trace metals in IC device fabrication

Semiconductor device fabrication requires strict control of sources of contamination; industry estimates suggest that contamination accounts for around 50% of yield losses. Metallic contaminants may be introduced via the wafer substrate or the chemicals and equipment used during the manufacturing process.

Monitoring and controlling trace element contamination begins with the high-purity wafer substrate. The substrate is usually silicon, but other materials such as silicon carbide, silicon nitride, and gallium arsenide are also used. High-purity electronic-grade silicon must be between nine nines (9N) and eleven nines (11N) – 99.9999999% to 99.999999999% purity. In terms of contamination, 9N purity means a maximum of one part per billion (ppb) of total impurity elements in the solid Si.

Trace metallic contamination in bulk silicon can be measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after dissolving the Si in hydrofluoric acid. Trace metals in the sliced wafer are measured using a surface analysis technique such as vapor phase decomposition, where the metals are extracted from the Si substrate into a droplet that is then analyzed by ICP-MS.

In addition to the high purity wafer substrate, the purity of chemicals used throughout the wafer fabrication process must be controlled to avoid introducing contaminants. Metallic contaminants are of concern because they can affect the electrical properties of the finished device, for example by reducing dielectric breakdown voltage – effectively causing a short-circuit. As well as contaminants dissolved in process chemicals, insoluble nanoparticles are also monitored throughout the manufacturing process.

ICP-MS in semiconductor manufacturing

When ICP-MS was introduced in the 1980s, it was of great interest to semiconductor manufacturers and chemical suppliers due to its high sensitivity, low detection limits, and multi-element capability. Use of ICP-MS for semiconductor applications increased rapidly in the 1990s, with the development of "cool plasma" on the HP 4500 instrument. Cool plasma allowed Na, K, Ca, and Fe to be determined at trace levels by ICP-MS, so semiconductor manufacturers and chemical suppliers no longer needed graphite furnace AAS to measure these elements. Being able to determine all required elements in one fast, multi element ICP-MS analysis provided significant benefits of improved turnaround time and sample throughput.

ICP-MS manufacturers have continued to improve the technique, a major development being the release of the Agilent 8800 triple quadrupole ICP-MS (ICP-QQQ), in 2012. The 8800 and its successor, the Agilent 8900 ICP-QQQ, provide higher sensitivity, lower backgrounds, and better control of interferences than single quadrupole ICP-MS. This allows a greater number of contaminant elements to be monitored at lower concentrations, including previously difficult elements such as Si, P, S, and Cl.

Table 1. Semiconductor process chemicals.

Process	Commonly used chemicals
Cleaning	Pure water, SC-1 (NH_4OH and H_2O_2), SC-2 (HCl and H_2O_2), SPM (sulfuric peroxide mix, a mixture of H_2SO_4 and H_2O_2), DHF (dilute HF), IPA (isopropyl alcohol), methanol
Developing	Photoresist, PGME (propylene glycol monomethyl ether), ethyl lactate, NMP (N-methyl pyrrolidone), TMAH (tetramethyl ammonium hydroxide)
Etching	HF, NH_4F, H_3PO_4, KOH, DMSO (dimethyl sulfoxide), MEA (mono-ethanol amine)
Polishing	CMP (chemical mechanical planarization) slurries, oxalic acid, NH_4OH

Silicon and other materials

Metal contamination in the silicon wafer substrate and associated layers and coatings can be monitored using surface metal extraction (SME) , also known as vapor phase decomposition (VPD). In the SME/VPD technique, the surface layer of the wafer (bare Si, or naturally or thermally oxidized SiO_2) is dissolved using HF vapor. The dissolved metals are collected by scanning a droplet of a recovery solution (usually HF and H_2O_2, but sometimes an alternative solution such as HCl/H_2O_2) across the wafer surface. The droplet is then pipetted from the wafer surface and transferred to the ICP-MS for analysis.

Other materials used in chip manufacturing are suitable for analysis using ICP-MS, including metal organic compounds such as trimethyl gallium (TMG), trimethyl aluminum (TMA), dimethyl zinc (DMZ), tetraethoxysilane (TEOS) and trichlorosilane (TCS). Such compounds are precursors used to grow thin metal films or epitaxial crystal layers in metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition. Pure metals such as Al, Cu, Ti, Co, Ni, Ta, W, and Hf are used as sputtering targets for physical vapor deposition (PVD) to create thin metal films on the wafer surface. High-k dielectric materials include chlorides and alcoxides of Zr, Hf, Sr, Ta, and the rare earth elements (REEs). Each of these materials has a limit for acceptable levels of contaminants, requiring analysis using ICP-MS.

Cleaning/etching and process chemicals

During IC fabrication, wafers undergo many processing steps, as illustrated in Figure 1. Chemicals used are in contact with the wafer surface, so control of contamination is critical. Examples of some commonly used chemicals are shown in Table 1.

Among the most critical process chemicals in terms of controlling contamination are ultrapure water (UPW) and the RCA Standard Clean (SC) solutions SC-1 and SC-2. The RCA cleaning procedure removes chemical contaminants and particulate impurities from the wafer surface without damaging the chip. SC-1 (NH_4OH and H_2O_2 in deionized water (DIW)) removes organic residues, films and particles from the wafer surface. SC-2 (HCl and H_2O_2 in DIW) then removes ionic contaminants.

> Return to table of contents
> Search entire document

Three Decades of ICP-MS Experience Drives Continuous Innovation

Working closely with leading semiconductor manufacturers and chemical suppliers since the late 1980s, Agilent has developed ICP-MS systems and applications that help to address the challenges of this fast-moving industry. From off-axis ion lenses and cool plasma to the unique, high-sensitivity 8900 ICP-QQQ with MS/MS operation, Agilent has been at the forefront of the key ICP-MS innovations critical to the industry.

Figure 2. The HP 4500 was the world's first computer controlled benchtop ICP-MS, introduced in 1994.

Agilent innovations

ICP-MS has been used by semiconductor manufacturers and suppliers since its introduction in the 1980s. But evolving industry requirements have led to demands for ever-higher analytical instrument performance. Working closely with the industry, Agilent has introduced many innovations to meet these evolving needs. These innovations address the demanding requirements of the semiconductor industry and are often of benefit for other applications of ICP-MS. The innovations include:

- The very high sensitivity offered by the off-axis ion lens systems of all Agilent systems.
- Cool plasma, available worldwide for the first time on the HP 4500 ICP-MS, gave the analyst a choice between graphite furnace atomic absorption spectrometers (GFAAS) and ICP-MS for in semiconductor applications.
- The small, benchtop design of the HP 4500 made it by far the most suitable system for clean room installations at that time.
- The low-flow, inert sample introduction system, available for all Agilent ICP-MS systems, controls contamination and provides the ability to handle very small sample volumes (such as <500 µL VPD droplets).
- A fully stainless-steel chassis and clean room preparation were introduced with the 7700 ICP-MS.
- Agilent 7900 quadrupole ICP-MS combines a high level of automation and ease of use with excellent sensitivity and low detection limits. Industry standard cool plasma operation and fourth generation collision reaction cell provide flexible and effective control of interferences.
- Control of reaction chemistry using MS/MS on the 8800 and 8900 ICP-QQQ, which provides unprecedented resolution of interferences.
- A low contamination gas flow path lowers detection limits (DL) on the 8900 ICP-QQQ Semiconductor (and Advanced Applications) models.

Agilent ICP-MS Solutions for the Semiconductor Industry

Agilent's global sales and support organization provides single and triple quadrupole ICP-MS systems specifically designed to meet the needs of the semiconductor industry.

Figure 3. The Agilent 7900 single quadrupole ICP-MS is ideal for the routine analysis of process chemicals and materials.

Figure 4. The Agilent 8900 triple quadrupole ICP-MS semiconductor configuration is designed specifically to meet the current and future needs of the semiconductor industry.

Single quadrupole ICP-MS

The Agilent 7900 ICP-MS provides high performance in a compact benchtop single quadrupole instrument. It is a cost-effective solution for measuring trace contamination in typical process chemicals and semiconductor materials. The 7900 has the performance and flexibility to handle most sample types, with options and accessories to allow the analysis of nanoparticles, organic solvents, and highly corrosive acids. It is a workhorse in many semiconductor companies and features:

- Industry standard cool plasma for low background equivalent concentrations (BECs) and detection limits (DLs) for critical trace elements, including Na, K, Ca, and Fe.
- Standard ORS^4 collision reaction cell (CRC) with helium (He) cell gas line for effective reduction of polyatomic ion backgrounds. This provides low DLs for interfered elements such as P, As, and Se.
- Option to add up to two further cell gas lines to support reactive cell gases such as H_2 and NH_3. H_2 reaction mode can resolve interferences including the intense overlap from N_2 on Si at mass 28. NH_3 reaction mode resolves difficult interferences such as the ClO overlap on V at mass 51, enabling V to be determined at ultra trace levels (BEC and DL of <3 ppt) in high purity HCl.
- ICP-MS MassHunter software provides an easy-to-use interface for method setup and routine operation, including preset methods to simplify method development for new users.
- The smallest footprint of any quadrupole ICP-MS (730 x 600 mm), minimizing bench space requirements in the clean room.

Triple quadrupole ICP-MS

The Agilent 8900 ICP-QQQ is a true triple quadrupole ICP-MS – a tandem mass spectrometer that uses MS/MS to control reaction chemistry, delivering low detection limits and reliably accurate results.

The 8900 #200 configuration is specifically designed for semiconductor applications, providing high sensitivity and low backgrounds, combined with a comprehensive range of interference removal capabilities. A proprietary cool plasma is included, together with the unique ORS^4 CRC able to operate in controlled reaction mode as well as He collision mode.

The 8900 ICP-QQQ uses the double mass selection of MS/MS to ensure that reaction processes are controlled and consistent, ensuring accurate analysis of trace contaminants in the highest purity semiconductor materials.

Setups for Different Sample Types

Handling organic chemicals

Many organic solvents and products are used in semiconductor manufacturing, including IPA (isopropyl alcohol), methanol, TMAH (tetra methyl ammonium hydroxide), NMP (n-methyl pyrrolidone), PGME (propylene glycol monomethyl ether), ethyl lactate, butyl acetate, and photoresist. Some organic chemicals are soluble in water, but often it is preferable to run the samples undiluted, both to minimize the risk of contamination, and to achieve the lowest possible detection limits. ICP-MS is suitable for the direct analysis of both water soluble and non-water-soluble organic samples. Non-water-soluble organics may be run direct, or diluted in a suitable solvent, for example xylene or toluene. Direct analysis of non-water-soluble organic samples requires some specific ICP-MS hardware and operating conditions, particularly for the sample introduction and plasma settings.

Solvent resistant sample introduction

Organic solvents may be incompatible with the normal peristaltic pump tubing of the ICP-MS. Self-aspiration nebulization avoids the potential for sample contamination from or damage to the pump tubing, while solvent resistant pump tubing is used for the spray chamber drain. A typical sample introduction setup for the analysis of volatile organic solvents such as IPA and NMP would include:

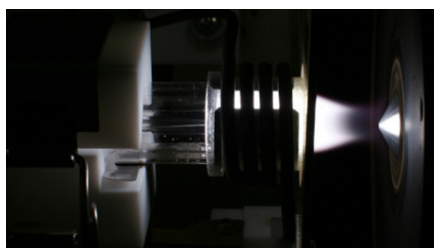
- Glass or quartz concentric nebulizer
- Quartz spray chamber
- Solvent-resistant drain kit
- Optional “organics” quartz torch with 1.5 mm i.d. injector (a torch with a 1.0 mm i.d. injector is also available, suitable for the most volatile solvents)
- Optional fifth Mass Flow Controller for oxygen addition to the carrier gas
- Pt-tipped sampling and skimmer cones

Control of vapor pressure

The high vapor pressure of some solvents can destabilize or even extinguish the plasma. All Agilent ICP-MS systems are fitted with a Peltier-cooled spray chamber to control solvent vapor pressure. The Agilent ICP RF generator is extremely robust and can easily tolerate the vapor pressure of even the most volatile solvents (such as acetone) at a spray chamber temperature of -5 °C. Some ICP-MS systems require extreme low temperatures (e.g. -20 °C) to tolerate such solvents.

Removal of carbon

When organic-based samples are analyzed, the high levels of carbon in the sample aerosol can lead to deposition of carbon (soot) on the sampling cone, causing instability and signal drift. To prevent carbon deposition, oxygen is added to the carrier gas to oxidize the carbon in the plasma. Oxygen (as a 20% oxygen in argon mix, for safety) is added using a fifth (option gas) mass flow controller, which is fitted as standard on the Agilent 8900 Semiconductor (and Advanced Applications)



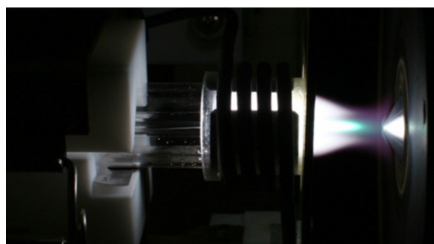


Figure 5. ICP-MS plasma appearance when aspirating aqueous solutions (top) and organic solvents (bottom).

ICP-QQQ models and is optional for other systems. When oxygen is added to the plasma, the plasma environment becomes considerably more reactive, so platinum-tipped interface cones should be fitted instead of the standard nickel cones. The Pt-tipped skimmer cone uses a different (brass) skimmer cone base.

Optimization of oxygen flow rate

Establishing the appropriate level of oxygen for a particular organic solvent is a simple procedure, as long as the operator has a clear view of the plasma (as provided with the viewing windows fitted to all Agilent ICP-MS systems). An initial flow of oxygen is added to the carrier gas flow (e.g. to give an oxygen level of 5% of the total argon carrier flow) and the organic solvent is aspirated at an appropriate flow rate. The oxygen flow rate is reduced slowly, until a buildup of carbon on the sampling cone is observed. The oxygen flow is then increased until the carbon deposits are decomposed and the green C_2 emission, visible in the central channel of the plasma, stops well before the sample cone orifice. This indicates that the organic matrix is being successfully decomposed.

The difference in the appearance of the plasma when an organic solvent is aspirated is shown in the photographs presented in Figure 5.

The upper photo shows the normal plasma appearance when aspirating aqueous solutions. The lower photo shows the plasma when aspirating an organic matrix (NMP), with insufficient oxygen to fully decompose the carbon. The green (C_2) emission zone extends all the way to the sampling cone tip and would lead to carbon disposition over time. When the O_2 addition is increased, the carbon emission zone retreats from the sampling cone tip. With sufficient (excess) oxygen, the green emission zone disappears completely, and the plasma appears almost the same as when aspirating aqueous solutions. It should be noted, however, that operating with an excess of oxygen addition will lead to shortened cone lifetime.

Once the optimum oxygen level for each solvent is determined, it can be saved in the acquisition method settings, allowing the correct flow to be set automatically for that sample type in the future. For a given solvent type, sample uptake rate and carrier gas flow rate, the oxygen addition remains constant and does not require routine adjustment. Table 2 shows typical oxygen flow rates and sample introduction configurations used for a range of solvents for which routine methods have been established.

Table 2. Recommended conditions for the analysis of various organic solvents.

Organic solvent	*Sample tubing id (mm)	Torch injector id (mm)	**O_2 flow (% of carrier gas)	**O_2 flow (mL/min)
Ethanol	0.3	1.5	3	35
PGMEA	0.3	1.5	3	35
Ethyl lactate	0.3	1.5	3	35
Kerosene	0.3	1.5	5	60
Methyl isobutyl ketone	0.3	1.5	8	100
Xylene	0.3	1.5	10	120
Toluene	0.3	1.5	12	150
Acetone	0.16	1	5	60

** Assumes a tubing length of 50 to 70 cm.*
*** For safety reasons, O_2 is added as a premixed blend of 20% oxygen in argon, so the flow rate required for the O_2/Ar mixed gas is 5x the amount shown for O_2.*

Sample introduction options for semiconductor samples

Agilent ICP-MS and ICP-QQQ systems can provide accurate trace level analysis of a wide range of chemicals and materials. Most samples can be analyzed using the sample introduction system included with the 7900/8900 Semiconductor (#200) configurations. However, some sample types are not compatible with the standard sample introduction system, so optional kits and components are available to allow such chemicals to be analyzed successfully.

The standard sample introduction system and interface of the Semiconductor configurations of the Agilent 7900 and 8900 comprise a PFA MicroFlow nebulizer, quartz spray chamber, quartz torch with 2.5 mm i.d. injector, Pt-tipped interface cones, and s-Lens. A summary is shown in Table 3, and full details are provided in publication number 5991-3780EN (Specifications for Agilent 7900 ICP-MS Semiconductor configuration) and 5991-7009EN (Specifications for Agilent 8900 ICP-QQQ Semiconductor configuration).

Table 3. Standard configurations of 7900 ICP-MS and 8900 ICP-QQQ Semiconductor models.

	Agilent 7900 (#200)
Nebulizer (concentric)	MicroFlow MFN 100 (PFA)
Spray chamber (Scott double-pass)	Quartz
Torch (with ShieldTorch System)	Quartz, 2.5 mm ID injector
Plasma Mass Flow Controllers (Ar)	4
Option gas line**	Option
Cool plasma capability	Supported
Interface cones	Pt (brass skimmer base)
Ion lens	s-Lens
ORS[4] cell gas line	1 (He)
2nd/3rd cell gas line (low- or high-flow rate options)	Option
EM detector dynamic range	11 orders
EM detector minimum dwell time in TRA mode	0.1 ms (100 µs)

	Agilent 8900 (#200)
Nebulizer (concentric)	MicroFlow MFN 100 (PFA)
Spray chamber (Scott double-pass)	Quartz
Torch (with ShieldTorch System)	Quartz, 2.5 mm ID injector
Plasma Mass Flow Controllers (Ar)	4 (supporting ultra-trace S and Si)
Option gas**	N/A (included)
Cool plasma capability	Supported
Interface cones	Pt (brass skimmer base)
Ion lens	s-Lens
ORS[4] cell gas lines	4 (He & 2 x high-flow & 1 x low-flow)
3rd/4th cell gas line (low- or high-flow rate options)	N/A (included)
EM detector dynamic range	11 orders
EM detector minimum dwell time in TRA mode	0.1 ms (100 µs)

***For alternative carrier or make-up gases such as 20% O_2/Ar for organics, or He for laser*

> Return to table of contents
> Search entire document

Figure 6. Inert (HF resistant), O-ring-free, PFA sample introduction system.

Sample introduction hardware required for particular sample types

Hydrofluoric acid

Trace (<0.1%) hydrofluoric acid (HF) can be tolerated for short periods by the standard quartz spray chamber and torch. However, when HF is analyzed as the concentrated acid (typically 38% w/w), or as a component of a wet etching bath or cleaning solution, etching of the quartz will occur. This leads to damaged components and sample contamination. The standard PFA nebulizer is tolerant of high concentrations of HF, but the standard quartz spray chamber, transfer tube, and torch must be replaced with HF-tolerant versions.

A complete PFA inert sample introduction kit (Figure 6) is available, with options for two different torch injector materials (Pt or sapphire). The Pt injector is often prefered for semiconductor applications, but sapphire is lower-cost and does not measurably increase trace element backgrounds. Two different internal diameters – 2.5 mm (standard) or 1.5 mm (used for organic solvents and nanoparticle analysis) – are available for each injector type.

Sulfuric acid

Sulfuric acid (H_2SO_4) is used in semiconductor cleaning processes. Mixed with hydrogen peroxide (H_2O_2) as sulfuric peroxide mix (SPM), it is used for degreasing and to clean organic residues from the wafer surface. The standard quartz sample introduction system is suitable for the analysis of sulfuric acid. However, concentrated H_2SO_4 has a very high viscosity of 27 centipoise and high specific gravity (1.84) at room temperature. This means that the concentrated acid (98%) is very viscous and does not aspirate or nebulize efficiently. Consequently, H_2SO_4 is diluted 10-fold in ultrapure water for analysis, giving an acid concentration of 9.8%. In addition, the standard Pt-tipped interface cone must be replaced with a Pt-tipped cone with a larger, 18 mm Pt insert*. This is required because the 9.8% H_2SO_4 aerosol forms a gel-like deposit around the tip of the sampling cone, which can etch and corrode the join between the Pt tip and the Cu base of the cone. Using the sampling cone with the larger diameter Pt insert avoids this type of corrosion.

Phosphoric acid

Phosphoric acid (H_3PO_4) has a viscosity of 65 centipoise which is 2.4 times higher than that of H_2SO_4 at room temperature. The very high viscosity of H_3PO_4 means that 100 times dilution in ultrapure water is required to allow successful aspiration for ICP-MS analysis. As with H_2SO_4, the Pt-tipped sampling cone with the larger Pt insert is required when analyzing H_3PO_4, to avoid corrosion around the cone tip.

** Agilent part number G3280-67056*

> Return to table of contents
> Search entire document

Automating Analysis of Metal Contaminants in Si Wafers

Agilent ICP-MS systems can be integrated with all leading automated VPD scanners to provide a fully-automated analysis of surface contamination on Si wafers.

Agilent ICP-MS and ICP-QQQ instruments are compatible with all leading VPD systems, including:

- IAS Inc., Japan
- PVA TePla AG, Germany
- NvisANA Co. Ltd, Korea
- NAS GIKEN, Japan

Figure 7. The WCS M300 automated VPD scanner system from NvisANA, Korea.

Vapor phase decomposition (VPD)

Metallic contamination of semiconductor devices may be introduced during cleaning, etching oxide growth, and ion implantation processes. Trace contaminants may also remain from the quartzite (sand) used to produce bulk, polycrystalline silicon, and the pure, monocrystalline silicon ingot from which the wafers are sliced. The main contaminant elements in quartzite are iron, aluminum, calcium, and titanium, while other elements may be introduced during the carbothermic processes used to convert quartzite into 98% pure silicon. Gas phase purification and chemical vapor deposition then remove most of the impurities, leaving silica of around eight nines (8N) purity.

Slicing and polishing the wafer can also introduce trace elements, for example from the chemical mechanical planarization (or polishing) slurries. The elements of most concern are the transition metals and alkaline elements, but their distribution in the wafer is not necessarily uniform. Iron can diffuse through the bulk silicon substrate into the surface oxide layer, while titanium impurity levels may vary due to segregation during melting and cooling of the monocrystalline Si ingot.

To ensure that metal contaminants do not adversely affect the IC device, the concentration of trace metals in the wafer surface must be determined. The bare silicon layer on the surface of the wafer quickly oxidizes to SiO_2 when exposed to atmospheric oxygen and water. This naturally oxidized layer is ~0.25 nm (one SiO_2 molecule) thick. 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 O_2 or water vapor. This thermally oxidized layer may be up to 100 nm (0.1 µm) thick. For both native and thermally oxidized SiO_2, the trace metals in the oxide layer can be measured at extremely low concentrations using vapor phase decomposition (VPD) coupled with ICP-MS.

Figure 8. The Munich Metrology Wafer Surface Measurement System (WSMS) manufactured by PVA TePla, integrated with the Agilent 8800 ICP-QQQ.

Figure 9. A fully automated VPD-ICP-MS system Expert PS manufactured by IAS Inc., integrated with Agilent 8800 ICP-QQQ. Image provided courtesy of ST Microelectronics, Crolles, France.

Combining ICP-MS and vapor phase decomposition

VPD-ICP-MS is a proven method of measuring trace metal contamination in silicon wafers. The VPD wafer sampling approach has good sensitivity because it concentrates the metals in the oxide layer from a large surface area of the wafer into a single droplet of solution for measurement.

The process (that can be completely automated) involves four steps:

1. The silicon wafer is placed in a VPD chamber, and exposed to HF vapor to dissolve the native oxide or thermally oxidized SiO_2 surface layer.
2. An extraction droplet (typically 250 µL of 2% HF/2% H_2O_2) is placed on the wafer, which is then tilted in a carefully controlled pattern so that the droplet is “scanned” across the wafer surface.
3. As the extraction droplet moves across the wafer surface, it collects the dissolved SiO_2, together with any contaminant metals.
4. The extraction droplet is transferred from the wafer surface to an ICP-MS or ICP-QQQ for analysis.

Advantages of coupling ICP-MS or ICP-QQQ with VPD

VPD can be performed manually, although it takes an experienced operator to get consistent recovery of the dissolved metals in the SiO_2 layer. VPD can also be coupled with a range of elemental analysis techniques to quantify metallic contamination. However, using ICP-MS or ICP-QQQ offers the advantages of high sensitivity and low detection limits for all required analytes, while automating the VPD process ensures consistency and reduces the potential for contamination.

Both the Agilent 7900 and 8900 ICP-MS instruments can be integrated with VPD systems for completely automated analysis of metallic impurities in silicon wafers. Both systems provide the good matrix tolerance required for analysis of thermally oxidized SiO_2, where the SiO_2 matrix concentration can be up to 5000 ppm in the extraction droplet (depending on the thickness of the oxide layer). The 8900 has the added benefit of MS/MS operation, providing the most effective of interference removal of any ICP-MS, and delivering lower detection limits and improved accuracy.

Expanding Capabilities with Accessories and Software

Figure 10. The Agilent I-AS integrated autosampler.

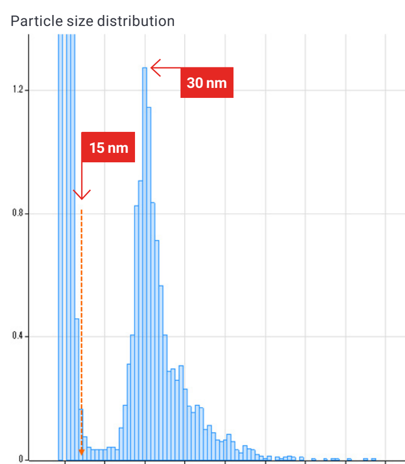


Figure 11. Size distribution of Fe nanoparticles (30 nm, 6 ppt) in butyl acetate by 8900 ICP-QQQ.

Integrated autosampler for Agilent ICP-MS

The Agilent I-AS integrated autosampler (shown in Figure 10) is compatible with both the 7900 and the 8900 ICP-MS instruments. It features inert parts for the sample probe and arm, short tubing length to allow self-aspiration, stainless steel and plastic components to minimize cleanroom contamination, and an integrated cover to minimize the risk of sample contamination.

The I-AS is also compatible with the continuous flowing ultrapure water (UPW) flowing rinse port option for the Organo Puric Omega (Puric ω) series UPW system (see contamination control section). Puric ω is currently only available in Japan, China, South Korea, Taiwan, Singapore, Malaysia, Thailand, Vietnam and Indonesia.

Nanoparticle analysis

To meet evolving requirements for higher integrated circuit (IC) performance and improved device yield, it is essential that contamination is controlled in the wafer substrate and on the surface of the device during fabrication. The nanometer scale of device features, currently 10 nm line widths, means that it may be necessary to monitor metallic nanoparticles (NPs) as well as dissolved metals in bulk chemicals and wafer processing and cleaning baths.

Agilent ICP-MS systems support fast time resolved analysis (TRA) to allow individual NPs to be detected and characterized, while the dissolved content can also be quantified in the same run. For applications where multiple elements are of interest, ICP-MS MassHunter software's Fast Time Program capability supports the acquisition of NP data for up to 16 elements from one visit to the sample.

The Single Nanoparticle Analysis software module available for ICP-MS MassHunter provides the method setup, analysis and data interpretation tools to simplify single NP analysis. The Agilent portfolio of NP solutions also includes support of Field Flow Fractionation (FFF)-ICP-MS for bulk characterization of samples containing multiple sizes and types of nanoparticles.

Online Monitoring of Metal Contaminants in Process Chemicals

Agilent ICP-MS systems can be integrated with automated online semiconductor process chemical monitoring systems from suppliers including IAS Inc., ECI Technology, and ESI.

Figure 12. The CSI online monitoring system from IAS Inc., Japan.

Figure 13. The ESI scoutDX automated online process monitoring system

Metal impurities in process chemicals are typically monitored at delivery (as part of acceptance criteria), at the central chemical supply, at distribution points, and at the point of use. Real time, online monitoring allows the immediate detection of metal contamination at all stages of the process. This, in turn, allows quick decisions to be made for process control and QA/QC purposes, and rapid assessment of the quality of chemicals awaiting off load from a tanker.

The Agilent ICP-MS and ICP-QQQ systems have been successfully integrated with the Continuous Chemical Sample Inspection (CSI) online monitoring system manufactured by IAS Inc, Japan (Figure 12). The CSI can sample multiple, remote liquid chemical streams, baths, or containers (e.g. tankers or drums).

The sample is delivered to the CSI via a dilution module. The sample flow rate is measured and a micro volume syringe pump then adds standard spikes to automatically generate a method of standard additions (MSA) calibration. MSA spikes are added to the continuously flowing sample, so analysis is very rapid. The system can switch between multiple sample streams, with an appropriate flush time between samples.

Urgent samples – for example from a delivery tanker – can be inserted into the queue and analyzed next. The CSI system integrates with Agilent ICP-MS instruments to provide an online monitoring system suitable for high purity chemicals. The design minimizes the potential for leaks or contamination, and is compatible with either self-aspiration or pumped sample flows.

The ESI scoutDX* on-line chemical monitoring system (shown in Figure 13) controls up to 20 remote sampling modules. Each module collects a small amount of a chemical or stream and transfers it to the central scoutDX system for ICP-MS analysis. Sample dilution and spiking are performed by a series of syringe pumps and switching valves, which prepare the sample for delivery to the ICP-MS nebulizer.

As well as enabling the rapid identification of trace element contamination, online process chemical analysis systems also reduce human contact with hazardous chemical samples, improving safety and reducing manual handling errors and contamination.

**Described in detail in Agilent ICP-MS Journal issue 69, July 2017.*

Contamination Control

The challenges of contamination control

- Semiconductor chemical analytical requirements require accurate analysis at low to sub ppt level, so even trace level contamination affects results.
- Many semiconductor analytes are common contaminants in laboratory infrastructure and equipment.
- Contamination can occur from vials and containers, sample handling, and from airborne dust.
- Insufficient knowledge of clean sample preparation and handling techniques causes variation in contamination levels.

Instrument environment

Agilent ICP-MS instruments can perform low-level analysis of a wide range of high-purity chemicals in different cleanroom environments. Class 1 and 10 cleanrooms are the cleanest and least prone to environmental contamination, but they are also the most expensive to design, build, and operate. These clean rooms are suitable for the production of semiconductor devices but are often not necessary or justified for laboratory analysis. However, it is increasingly common that the ICP-MS (especially the sample introduction area) is installed in a Class 10 or Class 100 enclosure inside a lower specification lab. This approach keeps the working area and samples clean, while reducing the costs of setting up and maintaining the main lab.

Class 1000 to 10,000 clean rooms and normal "clean" laboratories can also be used for successful trace-level analysis, but contamination incidents may be more frequent. User awareness and some key controls on the main sources of contamination can enable successful operation.

Critical requirements are:

1. Avoid contaminating the samples solutions from airborne dust by performing all sample preparation and handling in a clean bench. This is usually a fume hood type bench with a HEPA filtration system. Reducing dust/particle generating activities is also essential, for example by using powder-free nitrile gloves and removing dust-creating equipment (such as printers and water chillers) from the lab.
2. Avoid contaminating the samples from the reagents and laboratory equipment that comes into contact with the solutions. Key considerations are the vials and pipette tips, which must be metal free (no colored pipettes or vials caps, for example). The quality of ultrapure water (UPW) and acids used for sample stabilization or dilution is also critical (ultrapure reagents are recommended).

By implementing some of the methods, practices, and procedures in this document, it is possible to do low-level semiconductor sample analysis even in a class 10,000 cleanroom environment.

Tips for the analyst

Wear gloves at all times.

- Powder-free
- Rinse gloves with UPW prior to handling samples

Wear a mask.

Select a clean working area.

- HEPA filtered prep station
- Wipe the area with Deionized (DI) water
- Keep area clean after use

Some facts about cleanrooms:

- In a cleanroom, airborne particulates are controlled through continuous exchange of highly filtered clean air and through minimization of activities that generate particles.
- Air is supplied through HEPA filters (classified as having 99.97% efficiency at removing 0.3 µm particles) installed in the ceiling and extracted through grids and ducts on the floor. Air is forced through the laboratory with a high air exchange rate to dilute and remove particles. This design ensures that dust cannot collect on the floor and the air passing down through the laboratory is as clean as possible.
- A pressure gradient is set up between clean and less clean areas, so cleaner air always blows out to less clean areas, rather than the other way around.
- In addition to particle control, the temperature and humidity of the cleanroom are carefully controlled (70 °F or 21.1 °C, 45% relative humidity).

This type of air handling is expensive and cannot usually be retrofitted to an existing laboratory, so, in many facilities, it may not be an option to install such a system. In those cases, trace level analysis in high purity chemicals is still possible, but more care needs to be taken to isolate the samples from potential contamination from the laboratory environment.

Sample preparation environment

The most important area that impacts the contamination of semiconductor samples is the sample preparation environment. Use of a bench equipped with a laminar flow hood or workstation for preparation of standards and samples can significantly reduce the potential for contamination. Careful consideration must be given to the design and configuration of the hood, controls, switches, power, and water supply.

Working in a laminar flow hood

- Multiple workers operating in a single workstation at the same time increases the potential for contamination and creates a safety hazard.
- It is good practice to limit one person to a hood, especially when performing any sample preparation procedures that involve concentrated acids.
- Consider adding enough hoods to your clean-room design to allow each analyst to have their own workstation. This is also recommended when multiple incompatible chemicals are analyzed, such as concentrated acids and organic solvents. It is good practice to use separate work benches to ensure such chemicals are kept separate during preparation, storage, and disposal.

List of chemicals

These chemicals are commercially available, packed in 250 to 1000 mL PFA or FEP bottles.

Chemical	% composition
HF	38 to 51
HCl	20 to 35
HNO_3	55 to 70
H_2O_2	30 to 35
NH_4OH	20 to 28
H_2SO_4	93 to 98
$HClO_4$	60 to 71
HBr	44 to 49
$C_2H_4O_2$	30 to 99
PGMEA	

Tip: Some suppliers of high purity acids package their products in a PTFE container that is double bagged. There is an adhesive label on one of the bags. Remove the label from the outer bag and place it directly on the PTFE container.

Tip: The PTFE container often has an additional PTFE insert in the mouth of the bottle. Dispose of this insert immediately after opening the bottle, or rinse carefully with UPW before refitting to avoid contaminating the bottle.

De-ionized water: the most important reagent

Semiconductor fabrication facilities have site wide in-house UPW generation capabilities to support their specific manufacturing processes. These systems utilize large banks of ion exchange resin columns to clean the feedwater and produce an ultraclean final product. The UPW is usually piped to a tap or faucet in the laboratory for use in sample preparation, dilution and cleaning. The plant ion exchange columns are periodically replaced and, following replacement, the metal/ion levels can fluctuate in the UPW for a short time. For this reason, it is advisable to fit a high-quality standalone final polishing system in the laboratory to ensure a consistently pure water source. Suitable systems are supplied and supported worldwide, and well-known vendors include Merck (Milli-Q), Organo (Puric ω) and ELGA (LabWater).

A reliable supply of fresh UPW is essential for laboratories that measure trace contaminants in semiconductor chemicals. Note however, that the source water can quickly become contaminated through exposure to a poor quality or poorly cleaned container. For some elements, contamination can even occur through exposure to the laboratory air, which may affect solutions such as rinse bottles which are often left open for extended periods.

Laboratories in southeast Asia that use an Agilent ICP-MS system can make use of a novel rinse port developed by Organo for the Agilent I-AS autosampler, shown in Figure 10. The rinse port connects directly to the Organo Puric ω UPW system and supplies a constant flow of fresh UPW to the I-AS. This ensures that background levels in the rinse solution remain low, eliminating the possibility of carryover of contaminants from the rinse solution into the samples.

Tips:

- Monitor boron carefully in UPW as it is often the first element to break through an old resin bed when the ion exchange capacity has been reached.
- Always keep a high purity external source of DI water available.
- Acidify directly before analysis and where possible add acids by weight.
- Contaminants may leach from the container, so aim to analyze solutions as soon as possible after preparation.

High purity chemicals

High purity chemicals are required for most semiconductor analyses, either for standards or sample preparation. Chemical reagents with a metal impurity level below 100 ppt (pg/mL) or <10 ppt are recommended. This grade of chemical is best suited for use in a class 1000 clean environment or better. Care must be taken in the handling and use of these chemicals, since even in a class 10 environment they can be contaminated easily.

If high purity reagents are difficult to obtain, another option is to purify chemicals in-house using a sub-boiling point distillation system. Some chemical suppliers also offer a water standard for those laboratories without a source of UPW.

Steps to prevent contamination of high purity chemicals

Contamination control for high purity reagents is essential for ensuring the integrity of the subsequent analysis. A chemical handling/storage technique that works well to prevent the contamination of high purity reagents in the clean room laboratory environment is outlined here.

1. To minimize the risk of contaminating the reagent bottle: Each high-purity chemical generally comes in a PFA or FEP bottle, which has an additional inner lid in the neck of the bottle. Great care must be taken to avoid contaminating the entire bottle when opening this lid. Do not touch the lid even if wearing gloves. Instead hook the screw thread of the outer-cap under the edge of the inner lid and pull up the outer-cap, lifting the inner lid along with it. Once removed, the inner lid should only be reused after careful rinsing with UPW.
2. Decant (transfer) a suitable volume of the pure chemical to a second small clean container to act as the working solution. This reduces the risk of contaminating the entire volume of the new reagent in the original container. Use the following process to check the level of contamination in the secondary container to be used for storing the working solution:
   - Add 20 mL of an ultrapure 1% nitric acid solution to a 100 mL or 125 mL PFA container that has been cleaned according to the procedure described in "Inert lab-ware cleaning". Shake the container vigorously and leave to settle for 10 minutes.
   - Analyze the 1% HNO_3 solution into the ICP-MS as a sample, and monitor the analytical masses associated with environmental contamination. Elements typically include, but are not limited to, Na (mass 23), Al (27), Mg (24), K (39), Ca (40), Fe (56), and Zn (66).
   - If the observed count rates are equivalent to the counts for UPW alone, this would indicate no contamination in the cleaned bottle. If the count rates are significantly higher in the 1% HNO_3 than in the UPW, this shows that the vessel is contaminated. It should be returned to the beginning of the cleaning cycle. PFA is the best material to work with when performing low-level analysis. It contains no contaminant elements and is the easiest material to clean to low background levels both when new and when re-used.
   - If the secondary container bottle is contamination free, rinse out the 1% HNO_3 with UPW and then transfer the reagent to be used into the bottle. The 100/125 mL container will serve as a "secondary" reagent storage container. This will allow the original (or parent) 250 to 1000 mL reagent container to be opened the minimum number of times in its useful lifetime – minimizing the probability of it becoming contaminated.

Inert labware

Inert labware is manufactured from several different materials. Generally, there are two concentration ranges for semiconductor type samples, the ug/L (ppb) range, and the ng/L (ppt) range. For the ppb sample analysis range, inert labware can be made from polypropylene (PP), polymethylpentene (PMP, also known as TPX), or polyethylene (PE). For the ppt sample analysis range, inert labware should be made from PFA, FEP, or PTFE. Experience has shown that volumetric type labware is typically less useful in the semiconductor laboratory since most formulating work is done by weight.

Tip: Wide mouth bottles are the most convenient when working by weight. To arrive at a more exact weight, a PFA squirt bottle filled with the matrix being weighed out provides accurate dispensing.

Pipettes

Pipette tips are often overlooked as a source of contamination and even though they are probably the external device with the most contact with your sample.

- Use clear (not colored) pipettes, PFA if possible
- Use pipettes only when necessary – prepare solutions by weight where possible
- Rinse at least three times with a 10% HNO_3 solution and twice with the solution to be delivered before use
- Try to avoid pipetting concentrated acids. Where possible, make solutions by weight using a balance.

Should I use the same pipette tip or should I use a new one?

- Each new tip is a new source of contamination
- Use multiple deliveries of the same reagent when possible, starting with delivery to the highest-level standard, where any contaminants will have the least impact. Subsequent deliveries to lower standards will contain progressively lower levels of contaminants.

Automatic pipettes are calibrated with a precision >99% for 50 µL. 4 x 50 µL deliveries with the same tip will add up to <3% inaccuracy and will greatly reduce the chances of contamination. Always pipette the highest concentration first.

Inert labware cleaning procedure

A general rule is to clean labware with the same acid/reagent that the labware will contain for analysis on the ICP-MS, or with the industry standard cleaning solution (SC-2). For example, if a sulfuric acid manufacturer wanted to clean their inert labware, they would use a 5% sulfuric acid cleaning solution to do so. Most semiconductor facilities analyze almost all of the manufacturing acids, so try to use each set of labware for the same type of acids each time that material is analyzed.

The cleaning method employed in the lab depends on the level of analysis required. For example, device manufacturers may not need to determine metals at ultratrace levels (ppt), whereas manufacturers and distributors of process chemicals do.

Four separate cleaning chemistries recommended in textbooks on ultratrace analysis are as follows:

1. Soak all containers in 2 to 3 mol/L HNO_3 for at least a week, then rinse thoroughly with UPW. Drying is optional; some laboratories do not dry any labware.
2. Add HNO_3 to all containers and warm on a hotplate or in an oven at 50 to 60 °C for 8 hours. It is recommended that newly bought PFA or FEP containers are treated with this method.
3. Boil quartz labware in a solution of aqua regia (a freshly prepared mixture of 3:1 $HCl:HNO_3$).
4. A complete cleaning process used by labs that need to determine elements at the ultratrace level is to first clean containers with an alkaline detergent, rinse with UPW, clean with acetone, rinse with UPW, boil with concentrated HNO_3, and finally boil with diluted HNO_3. This process takes at least 10 days.

A common cleaning procedure is outlined below that is suitable for labs that need to measure trace contaminants down to ppt level.

Tip: The gloves worn by the analyst should always be rinsed with UPW before working with samples, calibration standards, or performing this cleaning procedure.

1. Rinse the container three times with UPW and pour contents to waste.
2. Prepare the necessary volume of the cleaning solution to fill all the containers to be cleaned.
3. Fill all the containers with the cleaning solution and replace the covers or caps.
4. Let the containers leach for one week, then invert the containers and allow leaching for another week. If there is a pressure buildup during the leach cycle, release the pressure by slightly loosening the cap, then retighten and continue with the procedure.
5. At the end of the cleaning cycle, pour the cleaning solution to waste.
6. Rinse the container out three times with UPW. If the cleaned container is to be stored prior to use, it should be filled with either UPW or 1% nitric acid.
7. Before using the container, rinse it three times with the chemical matrix the container will be used with.

Note that high quality PFA labware is expensive and should be reused where possible. A PFA bottle that has been used for a given reagent can be reused for that same reagent provided it is thoroughly rinsed and the previous sample was not heavily contaminated. Similarly, an empty bottle that contained a high purity acid can be rinsed and used for storage or preparation of other samples. Using the lowest practical calibration and spike levels helps to maintain low levels of elemental contamination of clean labware.

The purity of the acid used for cleaning is important. Ultrapure grade acid is not cost effective, while low grade acid risks contaminating the labware. If large volumes of acids will be needed, it may be cost-effective to invest in a sub-boiling distillation system. This can produce ultrahigh purity acids from lab grade starting material.

Cleaning smaller labware items

- Place all small objects such as pipettes and test tubes to be cleaned in the appropriately sized leach tank containing the cleaning solution.
- Allow to soak in the cleaning solution for 1–2 weeks.
- Before these items are used, they should be rinsed (three times) with UPW and then rinsed (three times) with the chemical matrix they will be used with. After these cleaning/rinsing steps, these items are ready for use.

Containers to be used as cleaning and storage tanks

- Polypropylene cleaning tanks should be cleaned thoroughly before they are filled with a cleaning solution. Cleaning solutions should be checked and replaced periodically to control contamination.
- Since the tanks usually reside in the clean room hood, be careful not to buy a size that is too large. Stacking containers help to optimize hood space.

ICP-MS instrument cleaning procedure

Before low level (ppt) analysis can be performed on an ICP-MS, the sample introduction system must be cleaned. Cleaning ensures the backgrounds are low and contamination problems are eliminated.

- All quartz sample introduction parts should be cleaned in 5% nitric acid overnight, or longer for ultrapure reagent analysis. Polypropylene and PTFE can be cleaned in more aggressive cleaning solutions that contain HF or H_2O_2. Do not clean glassware or quartz ware in solutions containing HF.
- The sampling and skimmer cones should be cleaned in 2% Citranox. HNO_3 (5%) can be used instead but the cones must not be exposed to acidic cleaning solutions for more than a few minutes and must be thoroughly rinsed afterwards.
- Nebulizers, especially when new, should be cleaned by aspirating a cleaning solution appropriate to the specific application. For example, if performing an analysis that uses HCl, use a dilute solution of HCl and HNO_3. A sulfuric acid manufacturer would aspirate dilute sulfuric acid to clean the nebulizer.

Sample and pump tubing

PTFE sample tubing

- 0.3 mm ID, Agilent part # G1820-65478. This tubing can be used for self-aspiration of solutions at a sample uptake rate of 200–300 uL/min, depending on sample type (viscosity) and tubing length. This tubing can also be used for pumped sample delivery, with appropriate peristaltic pump tubing.
- 0.2 mm ID, Agilent part # G1833-65573. This tubing can used for self-aspiration at a sample uptake rate of 50–150 uL/min. This tubing can also be used for pumped sample delivery, with appropriate peristaltic pump tubing.
- 0.15 mm ID, Agilent part # G1833-65572. This tubing can be used for self-aspiration at a sample uptake rate of 50 uL/min. This tubing can also be used for pumped sample delivery, with appropriate peristaltic pump tubing.

Peristaltic pump tubing: Peristaltic pump tubing is more easily contaminated and more difficult to clean than PTFE tubing, so pumped sample introduction is rarely used in semiconductor applications. However, when the use of pump tubing cannot be avoided, several different sizes (internal diameter) of pump tubing are available for delivery of different sample flow rates. Peristaltic pump tubing is more flexible and porous than PTFE sample uptake tubing and is more likely to contain trace metals that contribute to sample contamination.

Tip: Most semiconductor labs avoid peristaltic pump tubing, but self-aspiration requires more careful optimization as the flow rate depends on the sample type, the tubing length, and the nebulizer settings.

Cutting tools: Tools used for cutting sample introduction tubing should be made from ceramic or stainless steel. Normal mild steel scissors or craft knife blades will corrode and release metal oxide particles.

Sample preparation

In a normal laboratory environment (for example if a cleanroom is not available or justified) the possibility of sample contamination will be greatly reduced if all solutions are prepared in a clean bench/hood with a positive flow of high-efficiency particulate air (HEPA) filtered air. Wipe the bench area with DI water and rinse gloved hands before starting any sample preparation.

- Prepare at least three calibration standards, including the unspiked sample when standard addition calibrations are being used.
- Use the same pipette tip for delivery of all the additions of the calibration standard stock solution. Pipette the highest concentration standard/spike level (largest volume addition of the stock standard) first. This ensures that any contribution from contaminants in the pipette tip affects the highest standard level where the relative contribution of contaminants will be the lowest.
- For external calibrations or preparation of multiple samples for batch analysis, ensure that all vials are cleaned and ready at the same time.
- For standard addition calibrations, use of a low flow nebulizer permits the series of standard addition spikes to be prepared in a single 250 mL or 500 mL sample bottle. Each spike is added sequentially to the sample bottle while the sample is being aspirated, with the spiked sample being thoroughly mixed by swirling the bottle after each addition. Use of a single bottle and pipette tip minimizes the potential for contamination.
- Where possible, it is recommended to prepare samples by weight. Rinse the pipette tip a couple of times with 10% HNO_3 and then with the standard. To avoid excessive dilution of the sample, the total volume of spike additions should not exceed 1% of the sample volume – i.e. 2.5 mL total spike volume in a 250 mL sample.

Conclusions

Successful trace and ultratrace level elemental analysis depends on the combination of high-quality reagents and UPW, and a lab work area designed and operated to minimize contamination. These infrastructure controls must be combined with clean sample handling protocols and the correct optimization and operation of the ICP-MS instrumentation used to carry out the analysis.

There are potentially many sources of contamination during an analysis, so implementing good contamination control at all stages of the analysis has a direct impact on data quality.

Other Agilent Atomic Spectroscopy Solutions for the Semiconductor Industry

Figure 14. The Agilent 5900 Synchronous Vertical Dual View ICP-OES.

Figure 15. The Agilent 5800 Vertical Dual ICP-OES handles the toughest samples with confidence, giving the right answers the first time.

Agilent ICP-OES

ICP-OES is used in a variety of applications in the semiconductor plant, from QA/QC on reagents, to monitoring waste effluent prior to discharge to the environment. Effective analysis solutions are required for the detection of a variety of trace level pollutants generated during semiconductor fabrication. With Agilent's instrumentation, you can ensure the accurate quantification of metal pollutants, in matrices including organic solvents, acids, bases, and salts.

The Agilent ICP-OES utilizes smart tools to prevent time wasting instrument downtime and sample remeasurement. Agilent instruments ensure the highest levels of regulatory compliance and quality control in the analysis of semiconductor wastewater streams and can meet analytical performance criteria for regulatory environmental water analysis.

The Agilent 5900 is the world's smallest, fastest and most reliable ICP-OES. It needs only a single measurement per sample, capturing both an axial view and a radial view of the plasma at the same time—this is called Synchronous Vertical Dual View (SVDV). The 5900 is designed to handle the toughest samples, giving the right answers the first time with highest throughput and lowest cost of ownership.

The Agilent ICP-OES instruments can:

- Maximize productivity and reduce argon gas consumption by running axial and radial analysis at the same time for all wavelengths
- Achieve a sample to sample cycle type of <1 minute with the SPS 4 autosampler and AVS 7 switching valve
- Extend dynamic range and reduce interferences—easily ionised elements are automatically measured radially while other elements are measured axially. This capability allows % level and ppb level elements to be determined at the same time, in the same reading
- Ensure reliable and reproducible results, with excellent long-term stability, even with complex matrices such as sludge and wastewater
- Be setup even by inexperienced users, with a design that includes a plug-and-play torch and other features that don't require adjustment or alignment by the user
- Reduce sample uptake, stabilization times and rinse delays by using the Advanced Valve System (AVS) switching valve
- Allow you to see all elements in your sample (even the ones you didn't know about). This is done with a semi-quantitative tool called IntelliQuant, which rapidly finds up to 70 elements in a sample

When combined with the Agilent AVS 6/7 switching valve system, the IntelliQuant Screening software function can perform a full spectrum measurement in as little as 15 seconds per sample. This technique provides quick sample insight, which is useful when assessing samples to see if they are suitable for analysis using a different technique, such as ICP-MS or GFAA. When you know what elements are in your samples (and how much) you can avoid potential analytical problems, such as spectral interferences and measurement over ranges. This allows you to adjust your method or dilute your samples before you've wasted time measuring them.

Figure 16. The Agilent 4210 MP-AES.

Agilent MP-AES

The Agilent 4210 Microwave Plasma Atomic Emission spectrometer (MP-AES) features a plasma that is generated from air, offering ppb detection limits and is faster than conventional AA. Using air instead of acetylene or argon like other atomic spectrometers, significantly reduces the cost of ownership.

MP-AES is ideally designed for the analysis of metals in organic solvents such as Isopropyl alcohol (IPA)—used commonly as a drying solvent in the semiconductor industry. The nitrogen plasma allows for safe, reliable and efficient analysis and unattended operation, saving considerably on labor costs.

The 4210 MP-AES features:

- A vertically orientated torch, proven to minimize blockages, improving long term stability and reducing downtime, especially when handling difficult samples. End-on axial plasma viewing ensures excellent detection limits
- The External Gas Control Module (EGCM) accessory is specifically designed for the analysis of organic solvents, allowing for the automatic injection of air into the torch to prevent carbon build-up and reducing background
- Rapid method development using the simple user friendly MP Expert software
- Easy-to-use hardware including the torch loader handle that automatically aligns the torch and connects the gases, ensuring reproducible performance. This is coupled with the simple plug and play sample introduction components
- Remote control—addition of the Automation Software pack allows for remote control of the instrument, without user intervention

Figure 17. The Agilent 280Z AA.

Agilent atomic absorption

Graphite furnace atomic absorption spectroscopy (GFAAS) has long been used to measure trace levels of contaminants in semiconductor materials. GFAAS is ideal for manufacturers that require a cost effective measurement solution for only a few elements.

The Agilent 280Z AA graphite furnace atomic absorption spectrometer (GFAAS) provides the furnace performance and accurate background correction needed for ultra-trace level elemental measurements of samples related to semiconductor manufacturing.

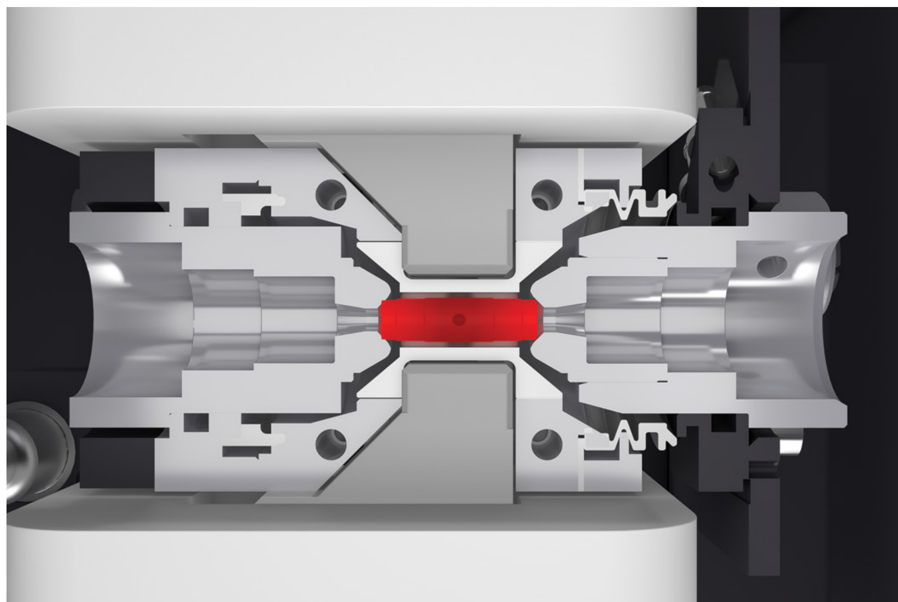
The instrument can even handle the complex matrices of chemicals used in the semiconductor industry. The 280Z features Zeeman background correction over the full wavelength range, well suited for the correction of the complex structured backgrounds, spectral interferences, and high background absorbances associated with those chemicals.

The 280Z also provides:

- High sensitivity and freedom from interferences at sub-ppb levels using the constant temperature zone (CTZ) furnace design which maximizes light throughput, ensuring the highest sensitivity
- High performance results from minimal sample volumes of a few microliters (µL), reducing the sample volume needed for measurements

The 280Z AA offers simple and economical determination of low level silicon (Si) in organic solvents such as PGME, PGMEA and NPA.

Semiconductor manufacturers and chemical supplies also use graphite furnace AAS to measure trace levels of Na, K, Ca, and Fe.



The Agilent Zeeman systems feature the transverse Zeeman configuration and constant temperature zone furnace design.

The 280Z AA features:

- Enhanced resolution—resulting from 1800 lines/mm diffraction grating along with a 330 mm focal length monochromator
- High analytical performance in tough matrices—comes from the high quantum efficiency photomultiplier tube (PMT) detector
- Highest sensitivity—geometrically optimized, Transverse Zeeman design allows for the removal of the most complex background signals while ensuring maximum light throughput through the system
- Maximum background correction accuracy—a unique magnetic waveform with smart polynomial interpolation offers double the speed of other systems
- Efficient sample analysis—long path length graphite tubes which are uniformly end heated leads to fast, efficient sample analysis
- Automated method development—unique surface response methodology (SRM) Wizard built into the SpectrAA instrument software helps ensure the optimum relationship between ash temperature, atomization temperature and analyte absorbance. The SRM Wizard simplifies method development and ensures that the right result is found in significantly reduced time

Learn more:
www.agilent.com/chem

Buy online:
www.agilent.com/chem/store

U.S. and Canada
1-800-227-9770
agilent_inquiries@agilent.com

Europe
info_agilent@agilent.com

Asia Pacific
inquiry_lsca@agilent.com

DE.2491203704

This information is subject to change without notice.

© Agilent Technologies, Inc. 2020
Published in the USA, July 29, 2020
5994-1841EN