Semiconductor Industry Benefits from ICP-MS

A lab director who helped pioneer the use of inductively coupled plasma-mass spectrometry tells why ICP-MS has become such an important tool for the measurement of metal contamination in the semiconductor industry.

ICP-MS is gaining expanded use in semiconductor fabrication due to its sensitivity and its ability to measure accurately up to 70 metals in a very short period of time.

As a laboratory serving the semiconductor industry, we now use ICP-MS to check nearly every chemical component or process used to process wafers or to which wafers have been exposed (see Table 1).

Since its introduction in 1984, great gains have been made in lowering detection limits using a quadropole mass spectrometer on the ICP. Suddenly, accurate measurements in the ppb-ppt level became possible.

It was soon recognized, however, that there was an argon-oxygen interference that made it impossible to measure low levels of Fe, Ca, and K, key elements that contaminate wafers.

Two alternatives have been developed to meet this challenge—graphite furnace atomic absorption spectrometry and magnetic sector ICP-MS (high resolution). Each has its own drawbacks.

To do both ICP-MS and GFAAS, for example, the sample, which may be as small as 0.1ml to 0.3 ml, must be split. This lowers the sensitivity that can be obtained and increases the possibility of contamination.

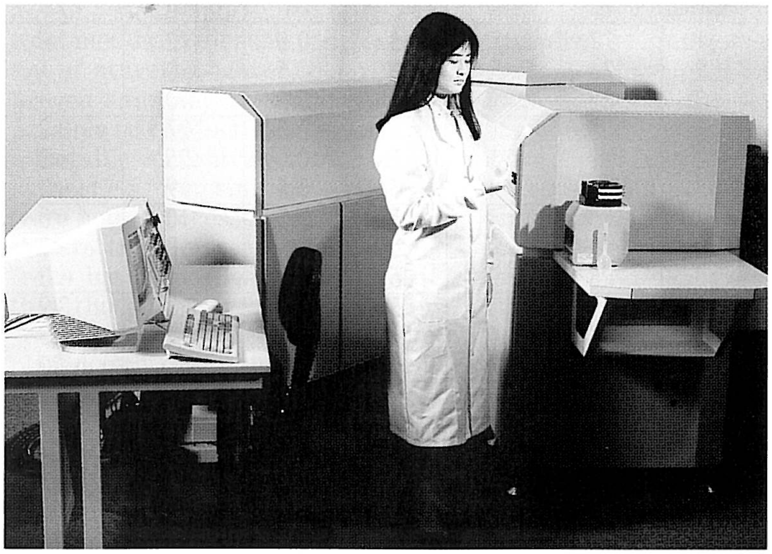
Table 1

Materials and Processes Tested for Metallic Contamination by ICP-MS

- Ultra pure water
- All chemicals used for: cleaning, drying, processing, etching, photolithography
- Wafers, whether bare or with SiO_2, Si_3N_4
- Special materials such as spin on glass, targets, metal films
- Processes such as ion implantation, chemical vapor deposition (CVD)
- Reactors
- Cleanrooms for metallic contamination in the air
- Cleanroom components including:
  Construction components
  Wafer carriers
  Gowns
  Elastomers used in equipment
  Plastics that are used in benches, etc.
- Ozone generators
- Gases: N_2, O_2, etc.

High-resolution ICP-MS (HR-ICP-MS) doesn't require splitting the sample, but it is slow if a lot of elements are to be analyzed.

One solution to the problem of argon interference and increased sensitivity is the use of innovative



The PlasmaTrace high-resolution magnetic sector-based ICP-MS, made by Fisons Instruments, has been installed at five semiconductor sites in the U.S.

Table 2

Metallic Specifications for Final Filter Water Quality (ppb)

Test	Attainable	Acceptable
Metal* by ICP-MS ppb		
Aluminum	0.007	0.05
Barium	0.002	0.01
Boron	0.3[1]	<2.0
Chromium	0.008	0.03
Copper	0.005	0.05
Iron	0.01[1]	0.10
Lithium	0.004	0.03
Magnesium	0.002	0.02
Manganese	0.004	0.03
Nickel	0.005	0.05
Sodium	0.01	0.06
Strontium	0.002	0.01
Zinc	0.008	0.06

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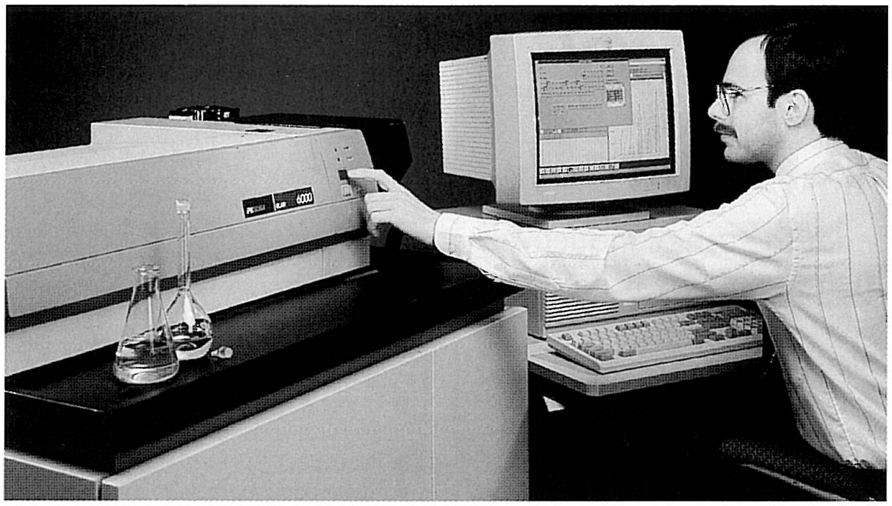
[1] Measured with special low-level test.



The ELAN 6000 ICP-MS from Perkin-Elmer Sciex Instruments (Thornhill, Ont.) comes packaged with multitasking Windows NT software.

injection systems on the front end of the ICP-MS.

New injection systems include the direct injection nebulizer, flow injection, ultrasonic nebulizer, and the membrane desolvator system. (See box, p. 54.) These nebulizers have distinct advantages for gaining sensitivity, but to obtain the greatest sensitivity per metal, often more than one front injection system is used.

The same is true for the ICP-MS injection configuration and the use of the quadrupole vs. magnetic sector instrument.

To obtain the data shown in the following applications, four different front-end systems and four different manufactured ICP-MS systems, including a high-resolution system, were used. The results shown are those that can be readily obtained, not necessarily the optimal results.

Water everywhere One of the most frequently checked materials used in the semiconductor industry is ultrapure water. Wafers are exposed to ultrapure water numerous times during processing. Any metal or metallic compound that doesn't favor staying in solution at pH ~7 can deposit out on wafers. When it does, it becomes mobile within the silicon and affects IC performance, often causing the circuit to fail.

Table 3

Trace Metal In Sulfuric Acid at a Sink Before and After Use (ppb)

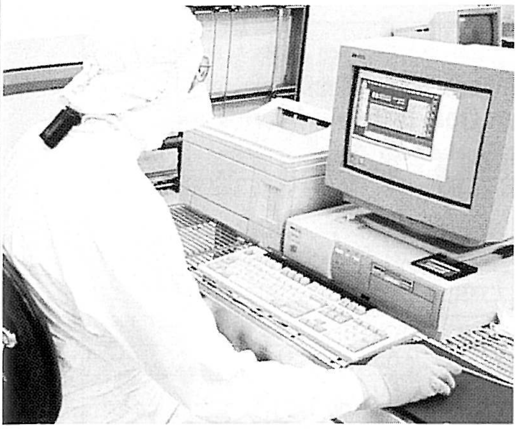
	Fresh Acid	After 300 Wafers	After 600 Wafers
Aluminum	3.4	4.1	13
Antimony	<0.1	0.4	0.4
Arsenic	<0.2	0.8	1.2
Barium	0.3	0.7	0.7
Beryllium	<0.1	<0.1	<0.1
Boron	<2	<2	<2
Cadmium	0.1	0.3	0.4
Calcium	16	65	90
Chromium	0.7	4.1	6.3
Cobalt	0.1	0.1	0.1
Copper	1.7	1.0	2.8
Gallium	<0.1	<0.1	<0.1
Germanium	<0.1	<0.1	<0.1
Gold	<10	<10	<10.0
Iron	<5	23	33
Lead	<0.1	3.6	5.2
Lithium	<0.1	0.1	0.2
Magnesium	1.5	31	41
Manganese	0.1	0.5	0.4
Molybdenum	0.2	0.7	10
Nickel	2.3	8.4	10
Potassium	<5	230	290
Silver	<1	<1	<1
Sodium	35	270	350
Strontium	<0.1	<0.5	0.5
Tin	<0.1	0.5	1.0
Titanium	3.0	3.8	4.0
Vanadium	<0.1	0.1	0.1
Zinc	1.6	5.5	7.3
Total	**66.0**	**653.7**	**867.6**

Table 4

Metal Impurities on 6-Inch Bare Silicon Wafers Measured by VPD ICP-MS

Surface Concentration ($\times 10^{10}$ atoms/cm^2)

Sources	#of Waters	Al	Cr	Fe	Ni	Na	Zn
A	1	77	<1	<5	<0.5	12	–
	2	76	<1	<5	<0.5	<10	–
	3	83	<1	<5	<0.5	10	–
B	1	9.4	<1	<5	<0.5	27	3.3
	2	11	<1	<5	<0.5	25	<3
	3	8.6	<1	<5	<0.5	19	<3
C (EPI)	1	<5	<1	<5	<0.5	<10	<3
	2	<5	<1	<5	<0.5	<10	<3
	3	<5	<1	<5	<0.5	<10	<3
D	1	8.5	<1	<5	<0.5	2.3	3.9
	2	<5	<1	<5	0.5	8.6	<3
	3	7.6	<1	<5	0.5	51	20
E	1	550	<1	77	1.3	<10	–
	2	611	<1	87	1.2	13	–
F	1	450	<1	50	1.9	30	–
	2	495	<1	65	1.9	14	–
G	1	260	<1	16	1.7	11	–
	2	270	<1	<5	1.4	8	–
H (8 in)	1	7	<0.5	<3	<0.3	24	62
I (8 in)	1	5	<0.5	<3	<0.3	<6	21



Hewlett-Packard's HP 4500 ICP-MS has been installed at Motorola, Sematech, and Balazs Analytical Lab.

Specifications for metallic levels of the more deleterious metals are shown in Table 2. Most semiconductor users maintain this level of purity 95% of the time, with an occasional drop as deionized resins deplete, during which time B, Si, and Na levels will be out of specification.

Metallic contamination in chemicals is also of great concern. Due to the ability to more accurately measure the sources of metallic contamination during manufacturing or bottling, chemical purity dropped from 750 ppb of total metals to <10 ppb in only three years.

Ultrapure, semiconductor-grade chemicals contain 1 ppb or less of any one metal and 10 ppb or less of total metals. With such a high quality of starting material and improved sampling procedures, it is possible to conduct studies such as a metallic concentration in a sulfuric acid cleaning sink where wafers were being processed (see Table 3). Wafers that were cleaned using a fresh bath were less likely to fail than those that were cleaned after several 25-wafer cassettes had been placed into the bath. Table 3 further illustrates how quickly a cleaning solution can be contaminated by the very product it is cleaning.

These results illustrate the need to replace cleaning solutions more often—a conclusion that can be attributed to our ability to make accurate measurements using ICP-MS.

Measuring residual metallic contamination on wafers after processing, but particularly after cleaning, has led to several methods for removing these metals from the wafer and placing them into a small volume of water or chemical solution so they can be analyzed by ICP-MS.

The need to measure residual metallic contamination on wafers after processing, but particularly after cleaning, has necessitated the development of several methods for removing these metals from the wafer and placing them into a small volume of a chemical solution so they can be analyzed by ICP-MS.

The most popular of these are vapor phase decomposition (VPD) and drop scan etching (DSE). VPD uses moist HF vapor to convert the metals to a soluble fluoride, while DSE uses nitric acid or a combination of acids. Table 4 shows the low-level metal measurements that can be made using these techniques in atoms/cm². One atomic layer is equal to 1 × 10^{15} atoms/cm².

One of the most interesting applications of ICP-MS in recent years has been to measure metals on bare silicon wafers and in both the oxide and nitride films deposited on them. By using extremely clean sample preparation practice, metals can be measured at 10^{11} to 10^{7} atoms/cm². Table 4 shows concentrations of metals on clean bare wafers from several fabs.

As Table 5 shows, there is not a linear concentration relationship between metallic impurities in a chemical and those that contaminate wafers dipped into them. In this case, wafers were dipped into

Table 5

Comparison of Trace Metal Concentrations in Hydrogen Peroxide Solutions and on 6-Inch Bare Wafers

	Concentration (ppb) Hydrogen Peroxide		Surface Concentration (x10^{10} atoms/cm²)	
	Sample A	Sample B	Wafer A	Wafer B
Aluminum	22	2.6	580	92
Chromium	3.3	0.1	<1	<1
Iron	6.7	<2	82	<5
Nickel	2.6	<0.1	1.2	0.9
Sodium	10	2.3	12	14

Injection Systems Boost ICP-MS Sensitivity

One reason inductively coupled plasma mass spectrometry has made such a hit in semiconductor trace metal analysis is the introduction of new injection systems that make ICP-MS even more sensitive.

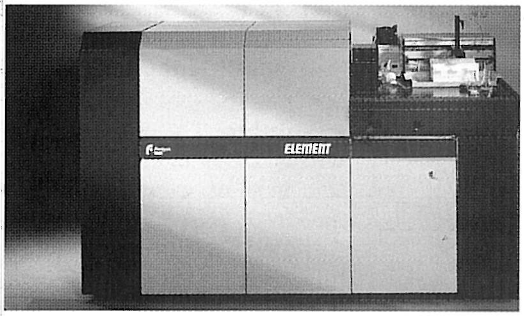
Leading the parade with clever front-end injection systems is CETAC Technologies, Omaha, Neb. Among CETAC's innovations are the following:

◆ The MDX-100 membrane desolvation system uses a microporous PTFE (polytetrafluoroethylene) membrane tube and Ar sweep gas flow to remove volatile species such as solvent water. This cuts the amount of hydrogen—and therefore hydrides like $^{238}UH^+$—in the sample stream.

◆ The Microneb 2000 direct injection nebulizer delivers the sample through a narrow capillary tube supported within a ceramic/sapphire nebulizer tip. The nebulizer geometry promotes interaction between the nebulizer gas and the liquid sample as they emerge from the end of the tip to create a fine mist with a narrow particle size distribution. This eliminates the need for a spray chamber, allowing the analyte to be directly injected into the central channel of the ICP.

◆ The U-5000 and U-6000 AT$^+$ ultrasonic nebulizers, when coupled with CETAC's AT$^+$ desolvation system, can improve detection limits by as much as a factor of 50.

Contact: Dan Wiederen, CETAC, 402-733-2829; fax: 402-733-5292.



Finnigan MAT's ICP-GD-MS adds an optional glow discharge ion source to the mass spectrometer.

Table 6

Typical Concentration of Metal Contaminants in Dielectric Oxide Films on Silicon Wafers from Different Sources

Concentration: ppm of oxide

Source	A	B	C	D	E (TEOS)	F (TEOS)
Oxide Thickness	3000	3000	3000	6000	2000	8000
Aluminum	2.9	1.2	16	19	0.2	7.3
Sodium	–	–	–	–	<0.4	0.93
Chromium	1.2	0.53	6.9	0.63	<0.02	–
Iron	4.6	4.4	12	3.0	<0.2	0.76
Nickel	2.3	0.68	4.5	0.56	<0.2	–
Manganese	–	–	–	0.11	–	–
Cobalt	–	–	–	0.01	–	–
Magensium	–	–	–	–	–	0.66
Zinc	–	–	–	–	–	0.18
Zirconium	–	–	–	–	–	0.02

two ultrapure hydrogen peroxide solutions. Although the results do show that the cleaner the chemical is, the less it contaminates the wafer, they also reveal that many metallic contaminants will concentrate on the wafer surface.

In Table 6, the concentration of metals is found to be quite high (ppm levels) in deposited SiO_2 dielectric films. These dielectric films were made using either silane (SiH_4 + O_2) or TEOS (tetraethylorthosilicate) chemistry. The results clearly show that TEOS films are far less contaminated than the chemical vapor deposition (CVD) film. Such data could have an impact on semiconductor processing procedures in the future.

Ion implanter While metallic contamination from reactors during wafer processing can be measured for any reactor, one of the more interesting reactors is the ion implanter, where it is important to measure unwanted elements that are implanted into the substrate during the ion implantation step. Since vapor phase decomposition and drop scan etching cannot penetrate the silicon to measure metallic contamination that occurs during this process, a new technique was developed.

A wafer with a thick oxide film is placed into the ion implanter with the other wafers that are processed. All of the metals, both desired and undesired, are trapped in this oxide. By dissolving this thick film and going through some appropriate preparation, the metals can be measured by ICP-MS.

Table 7

Air Quality at Various Fab Sites

Element in mg/m³	Class 100 Cleanroom Site 1 SC1/SC2 Cleaning	Class 100 Cleanroom Site 2 Final QA Room	Wafer Storage Room	Outside Cleanroom
Na	0.001	0.007	<0.001	0.1
Mg	<0.0007	0.001	<0.0007	NA
Al	<0.002	<0.002	<0.002	NA
B	0.063	0.026	0.026	NA
Ca	<0.07	<0.07	<0.07	NA
K	<0.1	<0.1	<0.1	NA
Fe	<0.01	<0.01	<0.01	NA
Ni	<0.001	<0.001	<0.001	NA
Cr	<0.0007	<0.0007	<0.0007	NA
Cu	<0.002	<0.002	<0.002	NA

Using this technique made it clear that there is a great deal of variation in the quantities of undesired contaminating metal from ion implanters. To date, the wafers measured have varied from 50 to 10,000 atoms/cm^2 of wafer. The elements most often found as contaminants are Al, Ti, Cr, Fe, Ni, Zn, and W, all of which are typical reactor components. This type of information is critical to the production of ICs.

Due to the extreme sensitivity of the ICP-MS instrument, metallic contamination can be measured in mini-environments or from cleanroom air, gases, and ozone generators. Table 7 illustrates the quantity of metals found while evaluating areas of a specific cleanroom.

Major role ICP-MS has not only been useful in the measurement of metals in a variety of situations, but also has allowed for a greater understanding of the sources, how and when they are transferred to semiconductor wafers, and at what levels they affect the product.

As a result, great advancements in purity of incoming and produced materials and cleanroom environments have been made. And without this tool, it will be very difficult to produce the next generation of integrated circuits.

—Marjorie K. Balazs

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