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KEEPING PACE IN CONTAMINATION MONITORING WITH ADVANCED **TECHNOLOGY**

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Keeping Pace in Contamination Monitoring with Advanced Technology

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Abstract

Shrinking device dimensions limit the level of contamination that can be tolerated on wafer surfaces. This trend sets more stringent requirements for both the purity of processing solutions as well as the fab environment. The paper presents data illustrating that state of the art analytical laboratory can keep pace with the new challenges of contamination control. Laboratories continue to provide critical information to aid the industry in its technology enhancements.

Introduction

The rapid development of semiconductor technology has challenged measurement science with increased demands for very low level contamination measurements. A new generation of analytical instruments to measure components in solution can successfully satisfy these increased requirements and thus wet chemical analysis continues to be the most reliable and accurate method for chemical measurements. The tremendous development in this area is best characterized by noting that detection limits have been reduced by factors of 10x to 100x below levels of just a few years ago. The "sub-ppb" (parts per billion) world of the early 90's have given way to a "sub-ppt" (parts per trillion) regime of measurement in the late 90's.

Key instrumentation and method improvements that are important to these advancements are:

- New inductively coupled plasma optical and mass spectrometry capabilities used for trace metal analysis
- New sample introduction technology in atomic spectroscopy
- Rapid improvement in ion chromatography used for anion and cation analysis
- Higher levels of automation reducing sample handling contamination
- Improved methods for processing samples that also reduce or eliminate contamination

Analytical measurement is not the limitation for improvement of ultrapure technologies. This is best demonstrated by actual analytical detection limits routinely measured in the laboratory and by new measurement methods providing ultra low level measurements for the semiconductor industry.

Advances in Analytical Instrumentation

Inductively coupled plasma (ICP) spectroscopy continues to be the work horse of trace metal analysis. Both optical or atomic emission (ICP-OES or ICP-AES) and mass spectrometry (ICP-MS) instruments have experienced dramatic improvements. Instrument size has typically decreased by a factor of 2-5, at the same time that the analytical performance has significantly increased. In both instrument families, a desk top unit can now offer a high level of analytical performance.

The new generation ICP-AES instruments have an axial view option with increased observation length and simultaneous multiple wavelength detection. The new CCD (charge coupled device) and CID (charge injection device) based detectors have increased linearity range and better background characteristics, thus offering lower detection limits. The major application of these instruments is for higher than 1 ppb metal concentration determinations, e.g., the analysis of dielectric and metallic thin films. Typical applications are the composition analysis of boron and phosphorus in BPSG films, titanium and tungsten in Ti-W films, and the trace metal contamination measurement of metallic thin films. These instruments are also usable for selected trace metal analysis work, exhibiting sub-ppb detection limits for certain elements.

ICP-MS remains the method of choice for very low level trace metal measurements. The new instruments offer increased linearity range (up to 10 orders of magnitude), lower instrument detection limits (even with conventional sample introduction methods), and new ways of analyzing elements that previously were undetectable because of interference from the plasma itself. Detection limits at ppt and sub-ppt levels for most elements are routinely attainable with these "fourth generation" ICP-MS instruments. Table 1 shows the everyday detection limit of an up-to-date ICP-MS instrument used for ultra pure water analysis under regular plasma conditions. The 'Average Detection Limit' column gives the two month average of daily detection limits and the 'Lowest Detection Limit' column gives the lowest daily detection limit observed. Detection limits are calculated as 3 times the standard deviation of all DI water blanks. While a few elements were not measured due to the high backgrounds (e.g., K interfered by ³⁸ArH⁺), increased instrument sensitivity allows measuring other ions, e.g. Ca, Fe and Cr from a minor isotope, thus avoiding the interference of ⁴⁰Ar⁺, ⁴⁰ArO⁺ and ⁴⁰ArC⁺, respectively. Detection limit determinations are statistical by their nature, however most of the numbers are less than 1 ppt, indicating exceptional analytical performance not seen on earlier versions of these instruments. Table 2 shows the detection limits of another new generation instrument with comparable performance.

Table 1.Daily Routine Detection Limits for Each Measured Element/Isotope in Ultra Pure Water During a Two Month Period with Ultrsonic Nebulizer - HP 4500 ICP-MS Using Regular 'Hot' Plasma Condiations.

Element Isotope <i>Li</i> 6	Detection L Average			Detection				
	Average	Lowest	Element Isotope	Average	imits (ppt). Lowest	Element Isotope	Detection	Limits (ppt)
1 11n	1.8	0.56	Ge 74	2.9	0.64	<i>Pr</i> 141	0.1	Lowest 0.01
Li 7	0.6	0.06	As 75	1.2	0.11	Nd 144	0.3	0.01
Be 9	0.0	0.00	Se 77	19.1	2.42	Eu 151	0.3	0.00
B 10	514	28	Se 82	430	2.42	Sm 152	0.2	0.04
B 10 B 11	483	20 19	Rb 85	0.1	0.04	Eu 153		
1			1				0.1	0.02
Na 23	20.7	2.33	Rb 87	0.3	0.06	Gd 157	0.3	0.07
Mg 24	2.1	0.18	Sr 88	0.1	0.01	Gd 158	0.3	0.06
Mg 25	2.4	0.42	Y 89	0.04	0.01	Tb 159	0.1	0.004
AI 27	1.3	0.33	Zr 90	1.2	0.01	<i>Dy</i> 163	0.2	0.04
Si 29	12611	1436	Nb 93	0.3	0.02	Ho 165	0.05	0.004
Ca 43	427	39	Mo 95	0.6	0.15	Er 166	0.1	0.03
Ca 44	315	40	Mo 98	0.7	0.10	Tm 169	0.05	0.02
Sc 45	0.9	0.08	Ru 102	0.2	0.02	Yb 172	0.2	0.03
Ti 48	0.2	0.02	Rh 103	0.1	0.02	Yb 174	0.2	0.05
<i>Ti</i> 50	10.7	1.82	Pd 105	0.3	0.09	Lu 175	0.1	0.01.
V 51	0.9	0.18	Ag 107	0.7	0.01	Hf 178	0.4	0.05
Cr 52	16.2	1.72	Pd 108	1.3	0.34	<i>Ta</i> 181	2.0	0.32
Cr 53	3.5	0.34	Ag 109	0.6	0.02	W 182	1.0	0.07
Mn 55	1.4	0.21	Cd 111	1.6	0.39	Re 185	0.4	0.06
Fe 57	223	18	<i>In</i> 115	0.1	0.02	Os 190	3.3	0.12
Co 59	0.2	0.03	Sn 118	6.7	2.21	<i>Ir</i> 193	0.2	0.06
Ni 60	1.6	0.16	Sb 121	0.5	0.12	Pt 195	0.5	0.11
Cu 63	0.9	0.13	Sb 123	0.8	0.10	Au 197	3.6	0.21
Zn 64	2.6	0.45	Te 125	2.9	0.84	Hg 202	7.5	0.38
Cu 65	1.0	0.13	Cs 133	0.1	0.02	TI 205	0.2	0.04
Zn 66	2.8	0.57	Ba 137	0.9	0.22	Pb 208	0.3	0.05
Ga 69	0.2	0.02	Ba 138	0.4	0.02	Bi 209	0.1	0.05
Ga 71	0.2	0.03	La 139	0.1	0.02	Th 232	0.2	0.05
Ge 72	3.1	0.65	Ce 140	0.1	0.02	<i>U</i> 238	0.2	0.03

Table 2.Typical Detection Limits for Ultra Pure Water Using Ultrasonic Nebulizer on a Perkin Elmer 6000 ICP-MS Instrument, at 1100 W RF Power.

Analyte	ng/L (ppt)														
Ca	40	Mn	0.9	Sr	0.04	Se	10	La	0.01	U	0.006	Pr	0.02	Yb	0.04
Li	0.3	Fe	50	Мо	0.4	Rb	0.02	Ce	0.009	Si	5000	Nd	0.06	Lu	0.02
Be	2	Co	0.1	Cd	0.2	Nb	0.08	Та	0.05	Ti	0.1	Sm	0.04	Hf	0.1
Na	9	Ni	0.2	Sn	2	Ru	0.04	Re	0.04	Ag	0.05	Eu	0.03		
Mg	1	Cu	0.2	Sb	0.2	Rh	0.02	Ir	0.04	W	0.04	Gd	0.07		
ΑI	2	Zn	0.5	Ba	0.06	Pd	0.08	Pt	2	Hg	1	Tb	0.02		
κ	40	Ga	0.03	Pb	0.06	In	0.02	TI	0.03	Os	0.1	Dy	0.04		
V	0.3	Ge	0.8	Zr	0.1	Te	0.4	Bi	0.02	Но	0.009	Er	0.04		
Cr	3	As	0.4	Sc	0.4	Cs	0.02	Th	0.02	Y	0.03	Tm	0.02		

Quadrupole ICP-MS instruments, at least in their earlier versions, were often not useful to analyze low levels of certain critical elements (e.g. Fe, Ca, K, Cr) due to the increased detection

limits caused by the increased background from Ar and some molecular species of Ar generated in the argon plasma itself. These interference's resulted in background equivalencies of 10 to 200 ppb in metal concentration levels. Actually, these interference's are at slightly different mass numbers than the target elements, but they cannot be resolved by a quadrapole mass analyzer. One of the most exciting new features of recent ICP-MS instruments is the so-called "cold plasma" mode of operation in which a stable plasma has been achieved at much lower power levels, thus generating lower levels of interfering species. Further, interface designs have been

Table 3.Achieved detection limits for UPW analysis by PE 6000 ICP-MS with USN cold plasma

Analyte	ppt	Analyte	ppt
Ca	30	Ga	0.7
Li	0.07	Sr	2
Na	8	Sn	8
Mg	0.8	Ba	20
AI.	2.4	Pb	0.6
K	20	Rb	0.9
Cr	0.9	Rh	2
Mn	8	In.	0.4
Fe	2	Cs	0.8
Ni	6	TI	0.4
Со	3	Ag	4
Zn	2	Bi	2
Cu	6		

improved to reduce secondary discharges within the mass spectrometer. Resultantly, interference's are significantly reduced and it is possible to measure traditionally interfered elements and some other high background elements with ppt levels of detection limits. Key elements with these lower detection limits are: Fe, Ca, K, Li, Na, Cr, and Ni. See **Table 3**, for typical detection limits of these elements in the "cold plasma" mode. **Table 4** lists the best attained detection limits observed for "cold plasma" conditions, (by quadrupole ICP-MS) both for long term and short term measurement periods. Note the levels for Fe, Ca, and K.

Table 4.Best background equivalent concentrations (BEC) and detection limits by 'shielded torch cold plasma' with concentric nebulizer on HP 4500 ICP-MS

	D	etection Limits (p	pt)		Detection Limits (ppt)			
Element	Average Average Long Term Short Term BEC n=24 n=6 or 18		Element	Average BEC	Average Long Term n=25	Short Term n=6 or 18		
Lithium	0.03	0.026	0.017	Cobalt	4.5	0.77	0.46	
Sodium	13	10	3.4	Nickel	1.3	0.57	0.41	
Magnesium	0.2	0.28	0.15	Copper	0.9	0.44	0.26	
Aluminum	0.2	0.46	0.02	Strontium	0.3	0.13	0.07	
Potassium	34	3.7	3.5	Tin	7.8	3.6	3.6	
Calcium	13	2.4	2.1	Barium	7.8	3.6	3.1	
Chromium	1.8	0.3	0.21	Lead	1.6	0.99	0.78	
Iron	2.2	0.4	0.25					

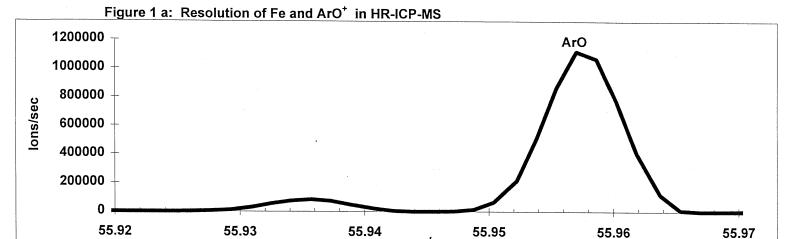
While challenged by new technology quadrapole instruments, the more complex and costly high resolution ICP-MS instruments have also experienced significant improvements. While possessing significantly enhanced resolution capabilities, these instruments have historically been plagued by significant stability problems. These issues have been addressed along with improvements in the ion throughput of the instruments, resulting in fine tools for specialized measurement situations. **Figures 1a-1d** show typical high resolution spectra that demonstrate the resolving power of these instruments.

Of equal importance to the advancements in the basic ICP-MS instruments, has been the development of several unique SIS (sample introduction system) devices that are used to introduce the sample solution into the plasma. There are two, somewhat contradictory goals of a SIS.

- 1. The sample should be introduced with high efficiency, so that a high percentage of the analyte elements are actually ionized in the plasma. Doing so enhances the instrument's sensitivity, reduces the sample amount required.
- 2. Other components of the sample solution, (i.e., acids, solvents, water, etc.) should have as little effect as possible. The key effects to be reduced are background interference from the matrix and signal suppression from the sample solution.

The most widely used SIS devices for trace metal analysis by ICP-MS are:

- The microconcentric nebulizer (MCN) that allows measurements with only a few hundred μL of sample solution.
- The direct injection nebulizer (DIN) which is virtually 100% efficient and can make measurements with as little as 2 µL of sample solution.
- The ultrasonic nebulizer (USN) which provides the highest analyte load to the plasma by nebulizing a high flow rate solution with 20-40% efficiency. Useful, when sample volume is not a limitation.
- The membrane desolvator (MDS) which actually removes solvent vapors and therefore decreases solvent induced interference's.



m/z

Figure 1 b: Resolution of Cr and ArC⁺ in HR-ICP-MS

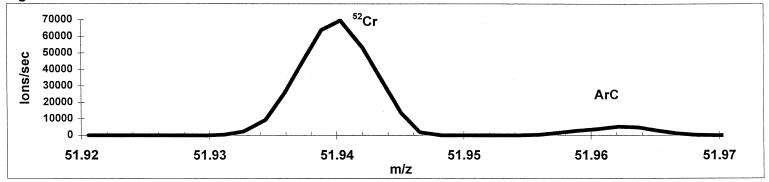


Figure 1-c:Resolution of Ca from interferences in HR-ICP-MS

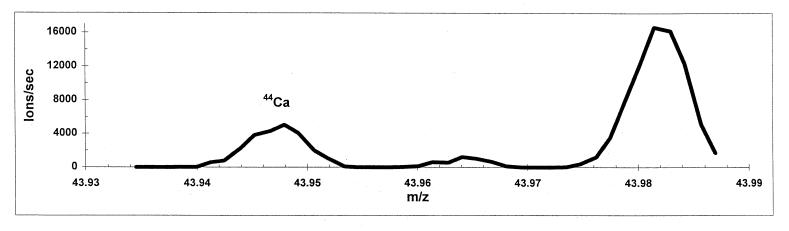
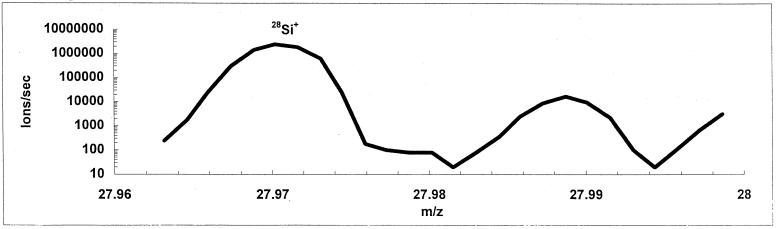


Figure 1 d: Resolution of ²⁸Si from CO⁺ and N2⁺ interferences in HR-ICP-MS



Other sample introduction systems, e.g., electrothermal vaporization, thermospray, etc. also have specific advantages, but are less frequently used than those listed above. In fact, the best results can be achieved by using a combination of these devices.

Applying the New Technology to Analytical Methods

The aforementioned advances in analytical instrumentation enable significant improvements in analytical methods. By combining the capabilities of improved ICP-MS instruments with new SIS devices, new regimes of measurement capability are possible. These attributes allow test methods characterized by very low sample volumes combined with very low detection limits. Specific test methods now possible include:

- The direct injection of selected chemicals with no need for intervening sample preparation steps such as preconcentration and/or matrix elimination. A small volume of the chemical can simply be diluted by ultra pure water and introduced into the measurement chain. The benefits of this approach are speed of measurement, avoiding potential contamination during the preparation process, and reducing sample volumes below the regulatory limits for special shipping and handling procedures.
- In the case of VPD (vapor phase decomposition) measurements of wafer surface contamination, these ppt and sub-ppt detection limits for test solutions combined with very low sample volumes (e.g. the scanning solution need not be significantly diluted) translate to 10^7 atoms/cm² detection limits or less on a 200 mm wafer surface for many critical elements. This capability provides the only measurement of surface contamination that can be directly standardized.
- In some cases, representative standards and blanks for the test matrix are not available and therefore the classic analytical technique of blank subtraction could not be used to complete the measurement. Because the BEC (background equivalent concentration) levels of these new instruments are so low and their ability to circumvent many measurement interference's, accurate determinations can be made even without such standards and blanks.

The Impact on Semiconductor Processing

These new analytical capabilities provide the foundation for new levels of reliable contamination control in the semiconductor industry. Measurements that are now possible include:

- Chemical contamination (i.e. beyond basic particle contamination) in clean room air can be detected at very low levels
- Dopant contamination on the wafer surface can be tracked
- Trace metal contamination on the wafer surface can be measured at very low levels
- Trace metals in DI water and process chemicals can be measured at sub-ppt levels

Table 5 shows detection limits of trace metals in clean room air as measured by ICP-MS after a special sample collection technique. The air sampler uses a scrubber to transfer metallic contamination from the air into solution. Similarly, anionic contamination can also be measured, e.g., ammonia, nitrate, chloride, sulfate, and fluoride. Detection limits for these measurements along with some sample test data are shown in **Table 6.**

Table 5. Detection limits of trace metal in clean room air

Element	(ng/m ³⁾	Element	(ng/m ³⁾
Aluminum	3	Lead	0.5
Barium	0.1	Magnesium	1
Boron	20	Nickel	2
Calcium	50	Potassium	10
Chromium	1 1	Tin	0.1
Copper	3	Titanium	2
Iron	3	Zinc	2

Table 6.Determination of Acid and Base Anhydrides in Air (Concentrations in ng/Liter)

			in the second discount of the second discount		the same and the s				
Analyte	DL	Wafer Cleaning	Shipping & Storage	Final QA Rm.	Analyte	DL	Wafer Cleaning	Shipping & Storage	Final QA Rm.
Ammonium	0.02	61	3	12	Phosphate	0.02	<0.02	<0.02	<0.02
Fluoride	0.3	28	2.9	10	Bromide	0.02	<0.02	< 0.02	<0.02
Chloride	0.006	0.14	0.14	0.045	Nitrate	0.01	3.1	1.6	0.94
Nitrite	0.006	33	6.9	9	Sulfate	0.02	0.14	0.51	0.16

Another interesting application example is the measurement of trace boron and phosphorus on the wafer surface. These contaminants are significant because of their ability to shift threshold voltages in completed devices. Accomplishing this determination requires sub-ppb detection limits from a very limited sample volume. Further, should such contamination occur, tracking down the source requires similar low level measurements of processing solutions, cleanroom air, process chemicals, packaging materials, etc. **Table 7** illustrates typical measurement capabilities for these elements.

Table 7.Measurement of Boron and Phosphorus by ICP-MS

	Boron	Phosphorus
Typical solution DL. in 2% HF (ppb)	0.03	0.2
Typical DL on 200 mm wafers in (10 ¹⁰ atoms/cm ²)	0.6	1.5
Typical concentration in clean room air (ng/m³)	10 to 200	

Current best achievable detection limits for VPD trace metal analysis on wafer surfaces is presented in **Table 8.** While additional development of sample preparation and handling techniques is required to make these measurements routinely available, the feasibility of very low level trace metal determinations in the 10⁷ to 10⁸ atoms/cm² range has been demonstrated.

Table 8.Achievable detection limit on 200 mm wafer surfaces.

Element	(10 ¹⁰ atoms/cm ²)	Element	(10 ¹⁰ atoms/cm ²)	Element	(10 ¹⁰ atoms/cm²)
Aluminum	0.02	Copper	0.005	Potassium	0.1
Arsenic	0.5	Iron	0.01	Sodium	0.02
Barium	0.001	Lithium	0.005	Tin	0.005
Boron	0.2	Magnesium	0.01	Titanium	0.01
Calcium	0.1	Manganese	0.005	Vanadium	0.002
Cobalt	0.002	Nickel	0.005	Zinc	0.05

Testing process chemicals for contaminants utilizing direct injection techniques is now possible with excellent results. **Table 9** shows detection limits for trace metals in 30% hydrogen peroxide measured in this manner.

Table 9.Detection limits of trace metals in 30% hydrogen peroxide solution using microconcentric nebulizer for direct sample introduction

Element	ng/g (ppb)	Element	ng/g (ppb)	Element	ng/g (ppb)	Element	ng/g (ppb)	Element	ng/g (ppb)
Aluminum	0.05	Cobalt	0.001	Magnesium	0.09	Rhodium	0.001	Vanadium	0.002
Antimony	0.01	Copper	0.02	Manganese	0.007	Rubidium	0.001	Zinc	0.03
Arsenic	0.005	Gallium	0.0005	Mercury	0.05	Silver	0.1	Zirconium	0.002
Barium	0.0008	Gold	0.01	Molybdenum	0.003	Sodium	0.1		4.7
Boron	0.05	Iron	0.05	Nickel	0.02	Strontium	0.0005		
Calcium	0.4	Lead	0.0008	Platinum	0.01	Tin	0.01		
Chromium	0.02	Lithium	0.003	Potassium	0.03	Titanium	0.02		

Conclusion

Semiconductor device technology is unique in terms of its continuous advances. Supporting the needs of this industry represents a continual challenge to the field of analytical chemistry, particularly the area of trace contamination analysis. New instruments and analytical methods have enabled the industry to meet this challenge.

Acknowledgments

The authors wish to acknowledge and thank Theresa Chu, Agota Fucsko, Hongjian Liang, Hong Khanh Ly and Yun Teng for running samples and compiling the data used in this paper.

Author Biographies

Janos Fucsko Ph.D., Research Chemist, joined Balazs in May 1990, where he studied the analysis of boron in BPSG and published on its anomalous behavior in the presence of HF. He also developed methods for the determination of trace metals in native oxide and dielectric oxide films using ICP-MS and other thin film analysis. Previously, he worked at the Hungarian Academy of Sciences in the Electroanalytical Research Group at the Institute of General and Analytical Chemistry, Technical University of Budapest for nine years where he was engaged in analytical chemical automation, flow injection analysis, electroanalytical sensors and monitors, and application of solution equilibria and kinetics in method developments for wet chemical analysis. He received his Ph.D. in Analytical Chemistry from the Technical University of Budapest in 1989. Dr. Fucskó is a member of the Society for Applied Spectroscopy, the American Chemical Society, and the Institute of Electrical and Electronic Engineers. He has seven publications.

John Mikulsky joined Balazs in July 1993 and is responsible for managing the development of the company's internal capabilities including analytical procedure development, computer systems, quality systems and specialized facilities. Most recently, he has led the effort to completely revamp Balazs' ICP-MS laboratory to become a state of the art analytical facility. Prior to joining Balazs, Mr. Mikulsky held several technical, marketing, and general management position at Raychem Corporation. He recieved his SM in Management Science from Massachusetts Institute of Technology, his MS in Electrical Engineering from Stanford University and his BSEE from Marquette University.

Marjorie K. Balazs is the founder and president of Balazs Analytical Laboratory in Sunnyvale, CA and Austin, TX. She has worked in the Semiconductor Industry since 1968. Prior to her work in the semiconductor industry, she spent ten years at Stanford Research Institute and taught for six years at the University of San Francisco (USF). She received her M.S. Degree in chemistry from USF and her M.A. Degree in chemical education at Stanford University. She is a member of ECS, ASTM, ACS, and SEMI/SEMATECH, where she is also on the Board of Directors. Outstanding honors include: Award from President Reagan in 1986 as an outstanding women entrepreneur; 1992 City of San Jose Small Business Award; and the 1993 SEMI Award for North America, recognizing her contribution in yield enhancement to the semiconductor industry over the past twenty-five years.