Can VPD/SME-ICP-MS Analysis Ever Be Made Routine?

Agilent Technologies

Presentation Outline

- Why is Surface Metal Extraction ICP-MS important?
- Technique
  - Wafer surface sampling
  - Analysis of the sample droplet
- Typical analytical figures of merit
  - Detection Limits (DLs)
  - Background Equivalent Concentrations (BECs)
  - Spike recoveries
- Validation of SME-ICP-MS methodology
  - Matrix effects / silicon suppression
  - Intentional contamination / extraction efficiency
- Conclusions / References / Website

Semiconductor Industry Trends

Metals contamination has become more critical as semiconductor devices move toward:

1) Higher operation speeds

2) Smaller feature and device sizes

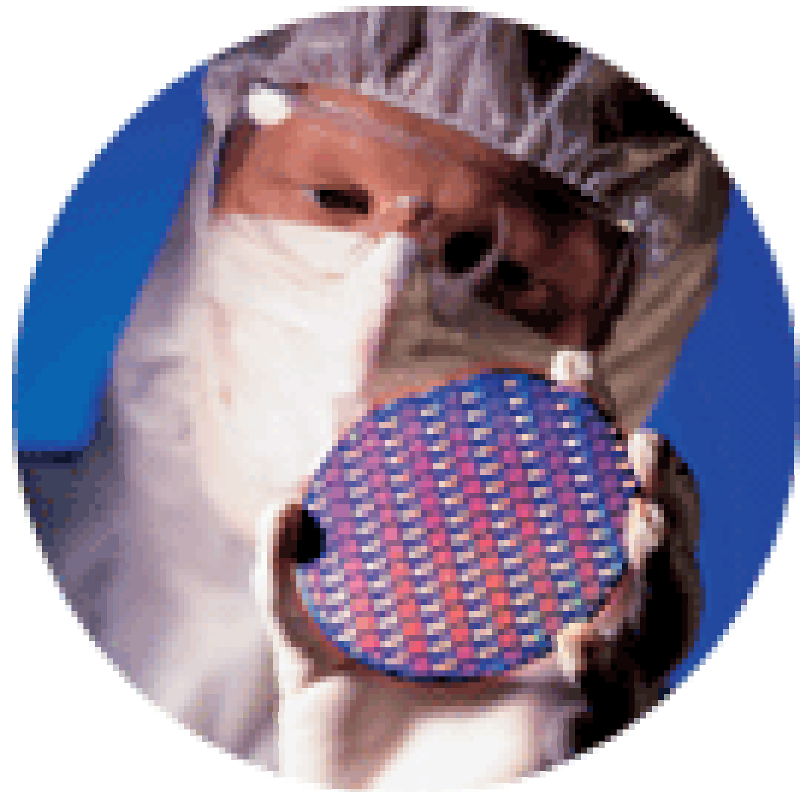
3) A larger scale of integration

4) Copper interconnect technology

Silicon Wafer and IC Device Manufacturing

- Semiconductor wafer and device manufacturing consist of a repetitive series of chemical and physical process steps

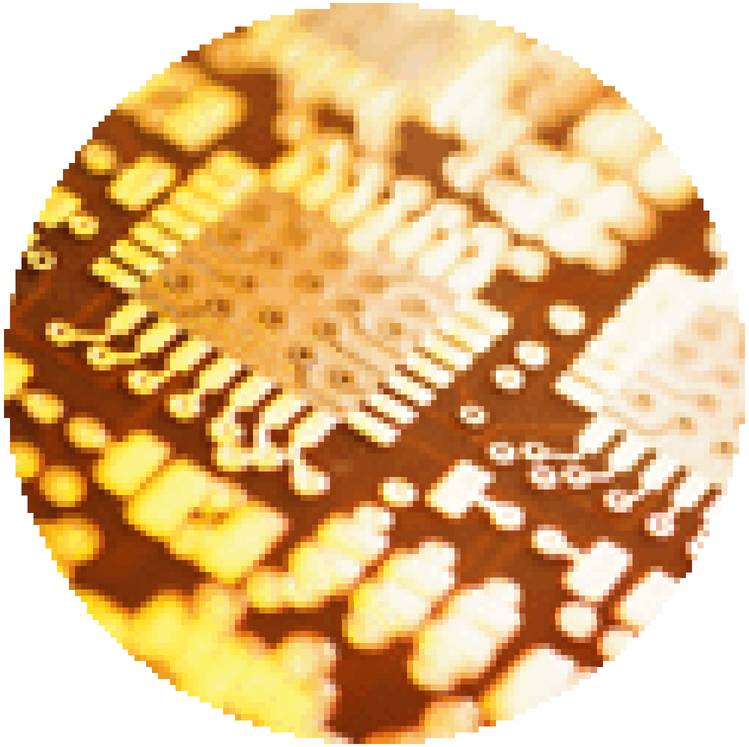
- Since most processes are chemical in nature, many possibilities exist to transfer and deposit chemical contaminants on silicon wafers, in thin films, at interconnects, or within the layers of an IC device



Agilent Technologies

Effects of Metal Contaminants

- They diffuse on the surface, in the substrate, and at interfaces leading to electrical defects and yield losses
- They can short out conductor lines and circuit interconnects, cause surface conduction, and decrease minority carrier lifetime
- Contamination accounts for over **50 %** of the yield losses in semiconductor manufacturing



Agilent Technologies

Challenges in Silicon Wafer Surface Characterization

- Sampling Challenges
  - Reproducible sampling of the wafer surface
  - Collection of the resulting sample
  - Metals extraction efficiency
  - Contamination control

- Measurement Challenges
  - Small sample volume (250 uL)
  - High silicon matrix and aggressive reagents
  - Requires ultra-trace detection limits
  - Potential for interferences

How is the Analysis Done?

- Surface Metal Extraction (SME) techniques are used to concentrate contaminants present in either the native oxide or the thermal oxide layer of the silicon wafer surface

- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is then used to determine up to 34 elements in a single 250 uL extraction droplet

- Typically a 20 minute turnaround for wafer sampling and analysis

SME-ICP-MS Technique

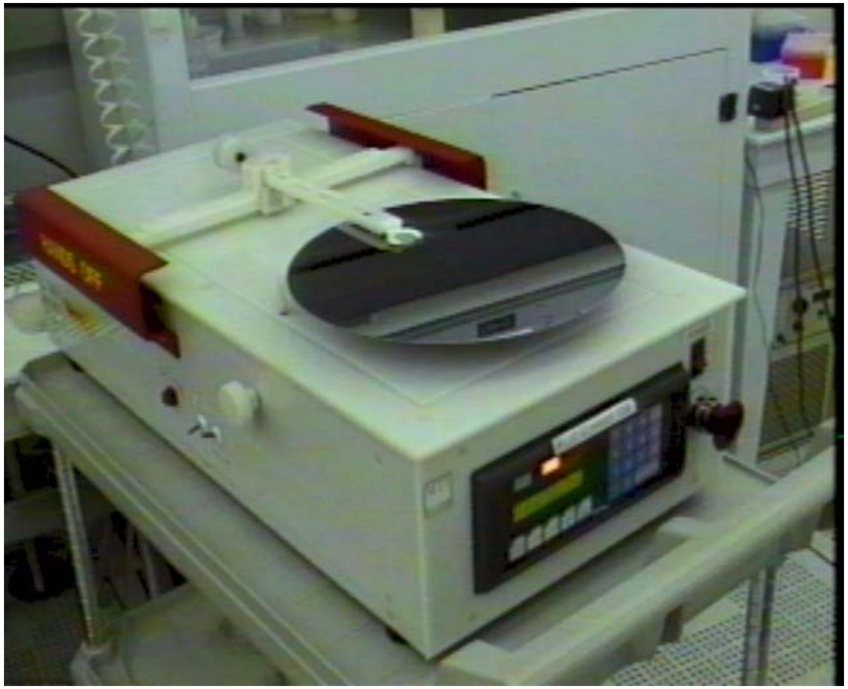
- SME efficiently concentrates contaminants from the wafer surface
- ICP-MS provides useful information on the type, source, and the levels of metallic contamination at virtually every processing step in semiconductor manufacturing
- Features:
  - Sub ppt detection limits
  - The ability to accurately calibrate and quantitate samples for up to 34 elements in a single extraction droplet
  - Enables real time wafer monitoring for quality control and process contamination control

Surface Metal Extraction (SME) Sample Preparation

- The wafer is exposed to HF vapor for 10 minutes to dissolve the SiO_2 layer on the wafer surface and 20 minutes for the thermal oxide

- The wafer is then placed on a wafer scanner where a 250 uL extraction droplet collects the contents of the dissolved SiO_2 layer

- The extraction droplet is deposited in an auto-sampler and analyzed by ICP-MS



SME Chemistry - Oxide Layer

- The primary chemical reaction occurs in an exposure chamber that is filled with hydrofluoric acid vapor. The reaction involves the decomposition of the oxide layer by the acid vapor as shown in Equation 1.

Equation 1

$$SiO_2\ (s) + 4HF\ (aq) \longrightarrow SiF_4\ (aq) + 2\ H_2O\ (l)$$

SME Chemistry - Trace Metals

- Metal contaminants in the oxide layer and on top of the crystal substrate undergo the following reaction to form soluble metal fluorides as shown in Equation 2.

Equation 2

$$CuO\ (s) + 2\ HF\ (aq) \longrightarrow CuF_2\ (aq) + H_2O\ (l)$$

SME Chemistry – Challenge

- Even with the acidic (HF) character of the SME droplet, metals more electronegative than silicon (Au, Cu, etc.) can “plate” out onto the wafer surface. Re-deposition to the wafer surface can occur through the following two mechanisms:

Electrochemical $2CuF_2\ (aq) + Si \longrightarrow SiF_4\ (aq) + 2Cu\ (s)$

Galvanic $Cu^{2+}\ (aq) + 2e^- \longrightarrow Cu(s)$

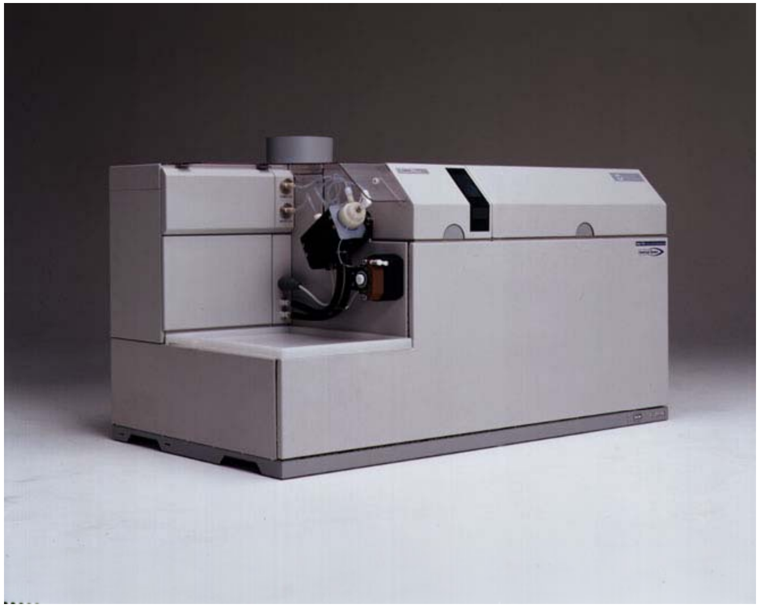
SME Chemistry - Solution to the Problem…

- Metal re-deposition to the wafer surface can be minimized by keeping the SME droplet chemistry highly oxidative. In the presence of hydrofluoric acid and hydrogen peroxide, these metals react to form a soluble fluoride.

H_2O_2 / Cu Reaction

$$Cu(s) + 2\ HF(aq) + H_2O_2\ (aq) \longrightarrow CuF_2(aq) + 2H_2O(l)$$

Agilent 7500s ICP-MS System



Open Architecture Sample Introduction System

•Easy access

•MicroFlow nebulizer facilitates self aspiration at 20 uL/min

New Omega II Lens System

•Superior Ion Transmission

•Lowest background ever!

Enhanced ShieldTorch System

•Long life shield plate

•Self aligning shield mount

•Cool plasma AutoTune

I-AS Autosampler

•Fully integrated

•Dynamic rinse station

•Covered for Ultra-trace analysis

Enhancing the Analytical Performance of the 7500s

- ShieldTorch System gives effective interference removal and sub-ppt DLs for virtually all elements
- Soft Extraction mode reduces the background to give a 10 – 100 fold increase in the signal to background ratio for most elements
- Use of a MicroFlow nebulizer, Peltier cooled spray chamber, wide bore torch injector, and highly efficient 27.12 MHz generated plasma ensure complete ionization of the sample matrix
- Flat mass-response curve of Omega II ion lens system is evidence of efficient analyte ion transmission to the quadrupole mass filter with the same high sensitivity across the entire mass range

Agilent's Multi-tune Software

- Switching between ShieldTorch System conditions and Soft Extraction mode is completely automated using Agilent's Multi-tune software
- Multi-tune allows complete data collection in a single acquisition
    - → This saves time
    - → Saves sample volume
    - → Reduces potential for sample contamination
- Auto-sampler probe samples each vial only once
    - ◆ Eliminates risk of contamination associated with multiple sampling
- All data is compiled in a single report
- Stabilization time in switching modes is minimal (20 seconds)

New, High Performance Nebulizer Technology

- The Agilent 7500 is designed to operate at low flow rates and new nebulizer technology matches this capability
- Very high efficiency nebulization means that better sensitivity can be achieved from very low sample volumes, by operating at flow rates of <100 uL/min
- The new Agilent Micro Flow all-PFA nebulizers are resistant to most acids and organic solvents

Analytical Capability

- By coupling a very high efficiency nebulizer (Agilent Micro Flow nebulizer) to a very sensitive ICP-MS system (Agilent 7500 operating under ShieldTorch Cool Plasma conditions), the current and future requirements of the semiconductor industry can be achieved.
- Calibrations at sub-ppt levels
- Quantitation and spike recovery at single ppt levels
- Limits of Detection at 10’s ppq

Agilent 7500 Performance Exceeds NTRS* Requirements for 2009

Element / Mass	No Silicon 7500 DL (ppt)	0.59 ppm Silicon 7500 DL (ppt)	450 mm Wafer DL (atoms/cm2)	NTRS 2009 Requirements
Li (7)	0.03	0.02	2.1 E6	<1.0 E11
Na (23)	0.20	0.27	4.2 E6	<2.5 E9
Mg (24)	0.17	1.00	3.4 E6	<1.0 E11
Al (27)	0.05	0.16	8.9 E5	<1.0 E11
K (39)	0.57	3.3	7.0 E6	<2.5 E9
Ca (40)	0.26	0.97	3.1 E6	<2.5 E9
Cr (52)	0.04	0.81	3.7 E6	<2.5 E9
Mn (55)	0.02	0.18	1.7 E5	<2.5 E9
Fe (56)	0.3	0.95	2.6 E6	<2.5 E9
Co (59)	1.4	0.58	1.1 E7	<2.5 E9
Ni (60)	0.74	1.0	5.9 E6	<2.5 E9
Cu (63)	0.25	0.14	1.9 E6	<2.5 E9
Zn (68)	0.86	3.0	6.1 E6	<2.5 E9

* National Technology Roadmap for Semiconductors

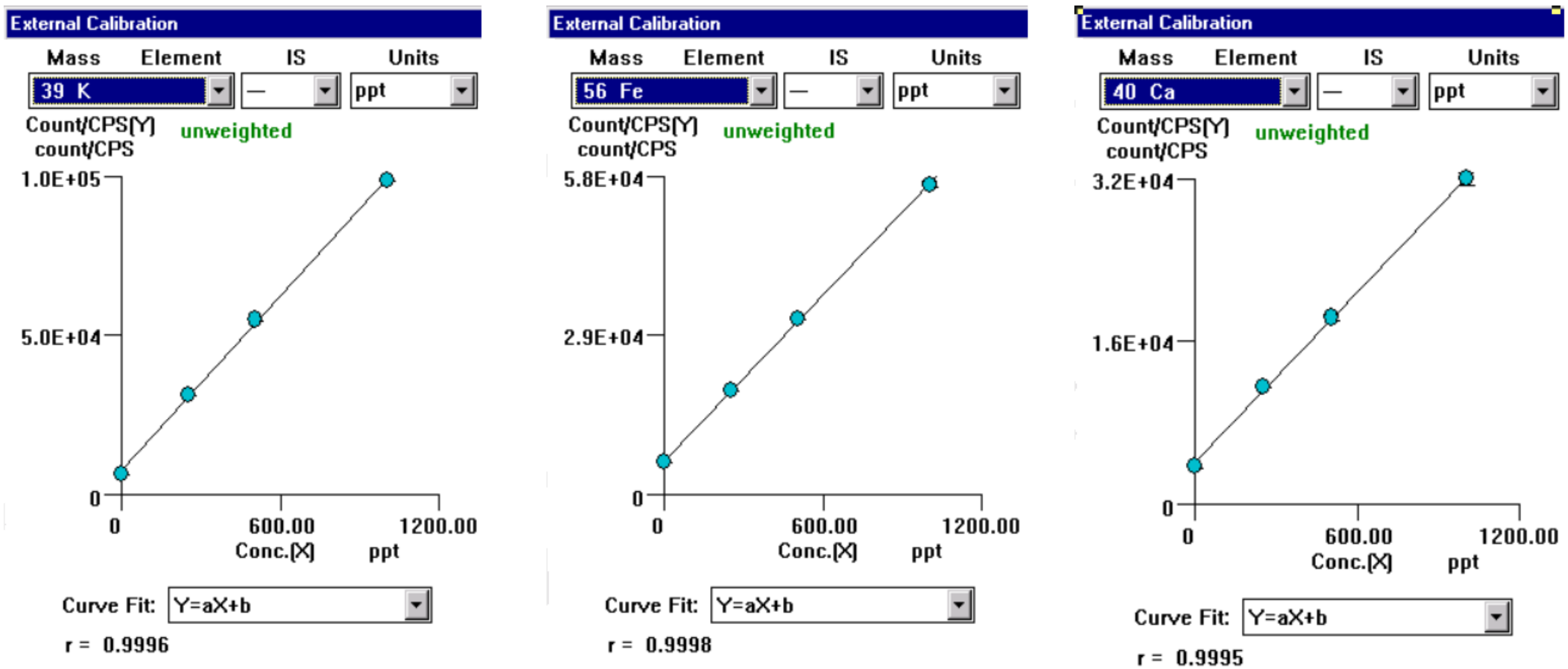
Comments on Detection Limit Results

- Exceptional performance for Ca, K and Fe
- A comparison of the detection limits measured in the calibration matrix and SME synthetic matrix show no significant differences
  - This highlights the effectiveness of the ShieldTorch interface in removing matrix-based polyatomic interferences
- Analytes e.g. Zinc, with a high ionization potential are effectively ionized in the high silicon matrix
  - This shows the effectiveness of the ShieldTorch System in eliminating matrix based interferences without loss of sensitivity
- 100 uL MicroFlow Nebulizer would further improve detection limits
  - These results were obtained using a 20 uL/min sample uptake

Background Equivalent Concentrations in the SME Matrix

Element (Mass)	No Silicon BEC (ppt)	500 ppb Si BEC (ppt)	Element (Mass)	No Silicon BEC (ppt)	500 ppb Si BEC (ppt)
Li (7)	0.07	0.06	Cu (63)	3	3.8
Na (23)	3.9	5.3	Zn (68)	2.8	3.8
Mg (24)	0.24	0.54	Zr (90)	0.9	0.6
Al (27)	1	1	Sn (118)	2.78	1.82
K (39)	25	36	Ta (181)	0.35	0.21
Ca (40)	22	36	Au (197)	1.55	0.69
Cr (53)	2.7	2.5	Pb (208)	1.4	0.72
Mn (55)	2.9	2.5			
Fe (56)	5.2	5			
Co (59)	4	4.3			
Ni (60)	0.9	1.3			

ICP-MS Analysis - K, Ca & Fe Calibration Curves in SME Extract



Elimination of Ar and ArO interferences on K, Ca and Fe respectively.

10 ppt Spike Recoveries in SME Matrix

Element	Mass	Conc (ppt)	% Recovery
Li	7	9.8	98
Be	9	11.0	110
B	11	9.5	95
Na	23	9.5	95
Mg	24	9.8	98
Al	27	10.3	103
K	39	9.9	99
Ca	40	9.6	96
Ti	47	10.8	108
V	51	9.9	99
Cr	53	9.4	94
Mn	55	10.0	100
Co	59	10.0	100
Ni	60	10.1	101

(SME matrix = 6% H_20_2, 5% HF)

…continued

Element	Mass	Conc (ppt)	% Recovery
Cu	63	9.9	99
Zn	68	11.5	115
Ga	69	9.9	99
Ge	70	10.6	106
As	75	9.1	91
Sr	88	10.2	102
Zr	90	10.3	103
Cd	111	9.5	95
Sn	118	10.0	100
Sb	121	9.6	96
Tl	205	10.0	100
Pb	208	10.0	100
Bi	209	9.9	99

Comments on Spike Recovery Data

- Excellent spike recoveries for all elements
  - Indicating negligible plasma ionization suppression from SME sample matrix
- The excellent recoveries also indicate the absence of any nebulization or transport interferences

Note: All recoveries were determined without the use of internal standards therefore simplifying sample preparation and eliminating a potential source of contamination

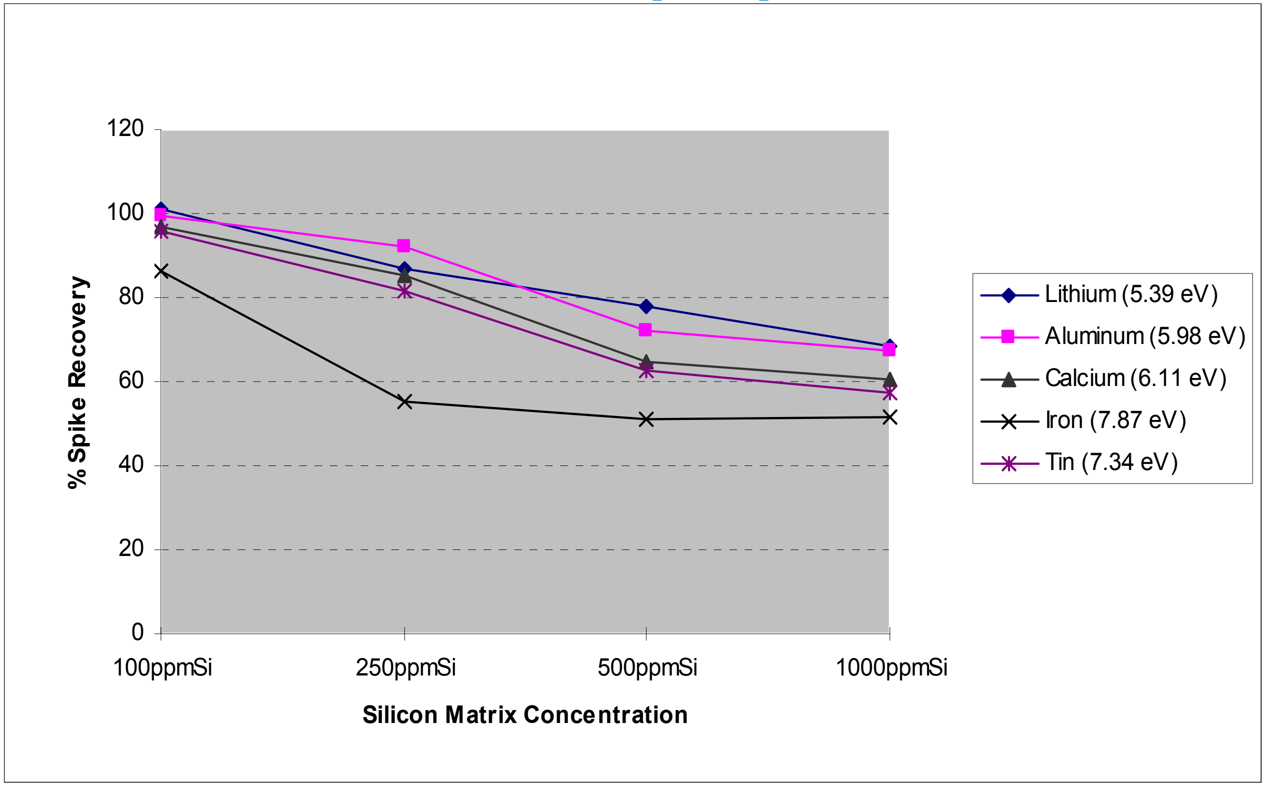
Review of Presented Results

- SME provides a fast and reliable method for the extraction of trace metals on silicon wafer surfaces
- Ion suppression and matrix interferences resulting from the silicon/chemical rich sample matrix are minimized through the unique design features of the 7500s
- Eliminates the need for:
    - MSA (Method of Standard Additions)
    - Matrix matching (Silicon)
    - Internal standards
    - Complex scanning reaction/collision cell technologies
- SME-ICP-MS can provide real-time analysis of wafer surfaces

Analytical Signal Suppression Experiments

- Purpose: Matrix effects resulting from the extraction sample matrix were evaluated to determine the extent of sample nebulization, transport, and plasma loading interferences. These results were also used to identify the concentration of silicon where suppression of the analytical signal begins.
- Method:
  - Prepare samples of extraction matrix with increasing levels of high purity silicon
  - Spike each level of silicon with the same concentration of trace metals standard
  - Monitor analytical signal suppression in each level of silicon matrix
  - Evaluate the use of internal standards for correction of signal suppression

Analytical Signal Suppression Results (100 to 1000 ppm Si) No Internal Standard (IS)

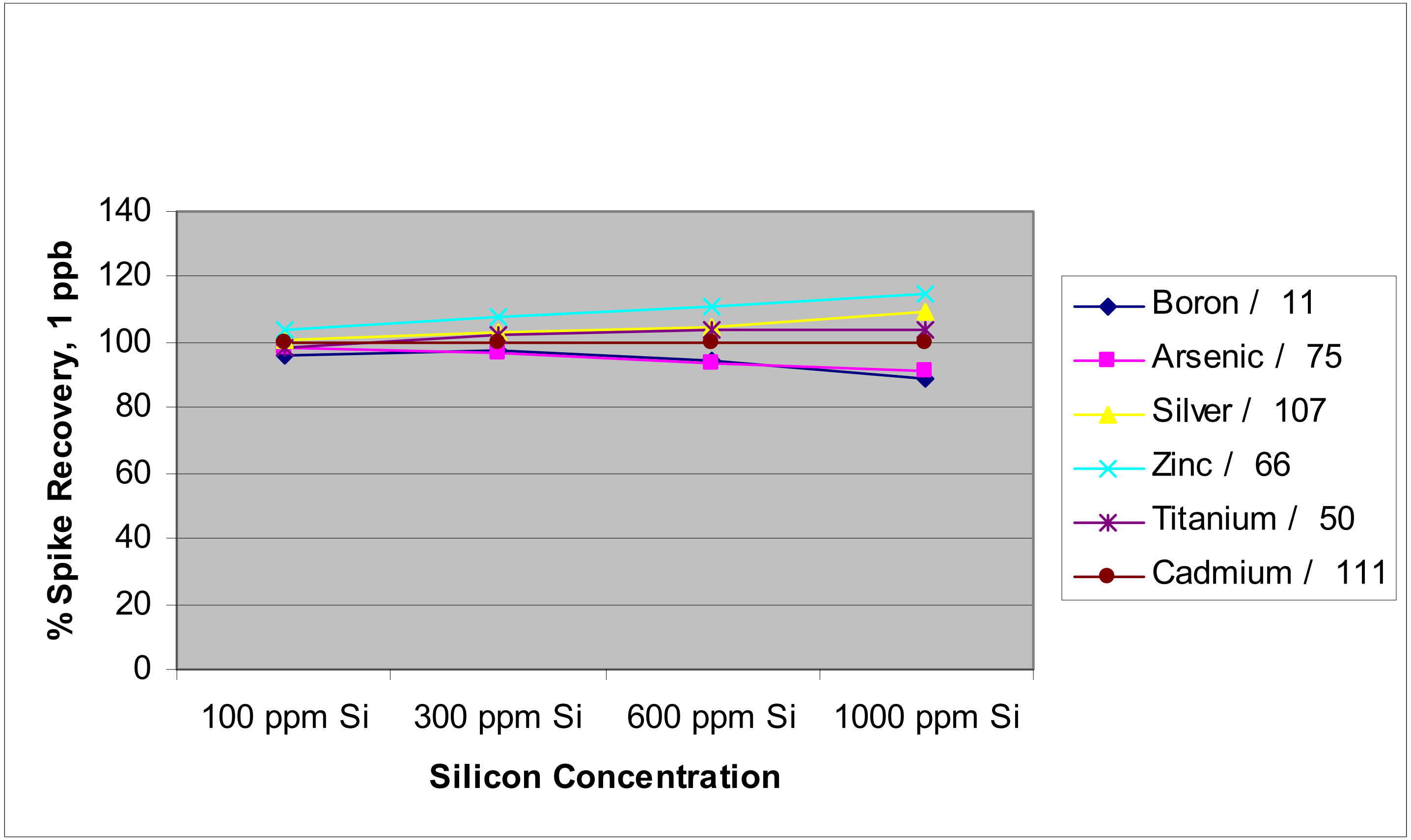


Ref: Huiling Lian, Beau Nicoley, Arnold J Howard and M A Radle, Silicon Wafer Thermal Oxide Metals Characterization by Surface Metals Extraction Inductively Coupled Plasma Mass Spectrometry (SME-ICP-MS), Semiconductor International, July 2000, Vol 34, p 217

Signal Suppression Observations...

- Data exhibits excellent spike recoveries for the extraction matrix containing 100 ppm silicon indicating minimal interference from the chemical extraction matrix
- Native oxide extracts contain less than 100 ppm silicon. This study proves that there are no suppression effects and no need to use internal standards when doing SME-ICP-MS on the native oxide
- The spike recovery data for the higher levels of silicon, typical in extraction samples of the thermal oxide, shows analytical signal suppression from the chemical matrix which is indicated by the lower spike recoveries
- The lower spike recoveries indicate either a reduction in the effective ionization potential of the plasma, “plasma loading”, or a nebulization interference. It’s possible that both interferences are present.

Analytical Signal Suppression Test, (100 to 1000 ppm Si) Using Internal Standards (IS)



Agilent Technologies

Internal Standards in High Silicon Matrices

- The analytical signal suppression observed in the higher levels of silicon, typical of the thermal oxide layer, can be corrected for using internal standardization.
- Recommended technique for measuring the thermal oxide layer
- Contamination associated with the use of internal standards can be avoided by improved lab technique, the use of high concentration internal standards (1000 ppm), and small volume spikes (50 uL)

Summary of Signal Suppression Experiments

- The native oxide layer which contains < 100ppm silicon is routinely analyzed for trace metal contaminants.
  - No signal suppression
  - No internal standards
- The thermal oxide layer, which is less frequently monitored, contains > 100ppm silicon.
  - Moderate suppression
  - Correctable with internal standards
- Both applications can be routinely addressed by SME-ICP-MS

Intentional Contamination of Silicon Wafers

- Purpose: An intentional contamination study was done to assess the extraction efficiency of removing trace metals from the silicon wafer surface. A standard clean 1 (SC1) cleaning bath was used to deposit trace metals onto silicon wafer surfaces.
- Method: An SC1 formula was prepared at the following concentration; 1% NH_4OH, 1 % H_2O_2, 98 % DI H_2O
- The SC1 formula was then spiked with a multi-element standard at 200 ppt
- The SC1 was the poured onto the surface and the wafer exposed for five minutes and then blown dry with nitrogen
- Successive extractions were performed to asses extraction efficiency

Metal Extraction Efficiencies - Intentional Contamination

Element (Mass)	Extraction Drop 1 Conc (ppt)	Extraction Drop 2 Conc (ppt)	Extraction Efficiency (%)
Li (7)	74	2	97.4
Be (9)	1830	1	99.9
B (11)	1040	18	98.3
Na (23)	297	5	98.3
Al (27)	2740	6	99.8
K (39)	319	1	100.0
Ca (40)	170	1	100.0
Ti (50)	190	1	100.0
V (51)	63	1	100.0
Cr (52)	73	1	100.0
Mn (55)	130	1	100.0
Fe (56)	1430	27	98.1
Sr (88)	100	1	99.0
Ni (60)	130	1	100.0

Metal Extraction Efficiencies - Intentional Contamination Continued

Element (Mass)	Extraction Drop 1 Conc (ppt)	Extraction Drop 2 Conc (ppt)	Extraction Efficiency (%)
Cu (63)	2950	28	99.1
Zn (68)	3900	1	100.0
Ga (69)	3510	8	99.8
Ge (72)	74	1	98.7
As (75)	66	1	100.0
Zr (90)	443	5	98.9
Nb (93)	75	4	94.9
Pd (105)	83	3	96.5
Cd (111)	840	20	97.7
Sn (118)	2410	90	96.4
Sb (121)	84	2	97.7
Ba (137)	84	3	96.6
Pb (208)	3610	8	99.8

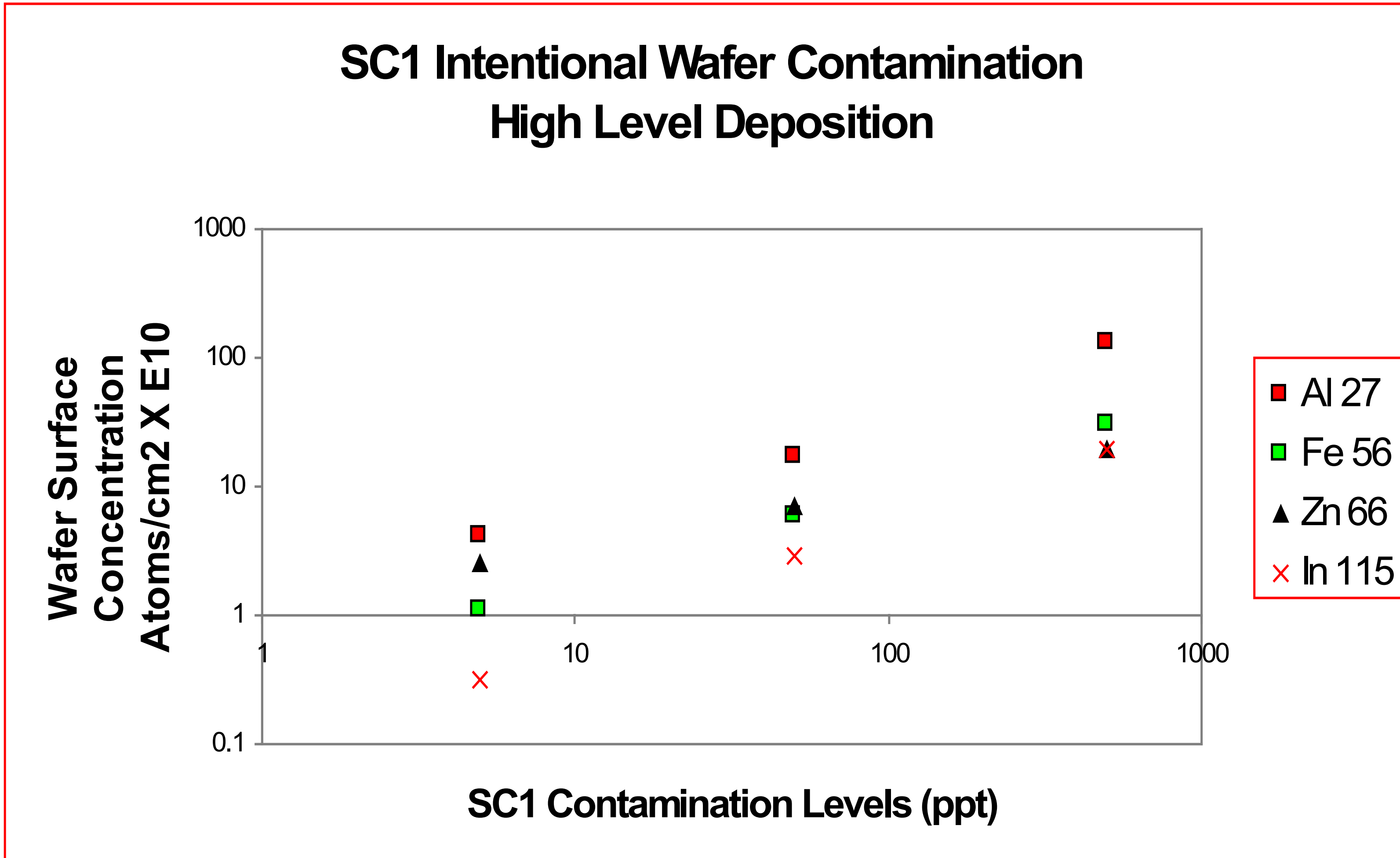
Summary of Intentional Contamination Study

- The extraction efficiency demonstrates excellent recoveries from the wafer surface
- 33 Elements were spiked into the SC1 solution, all except Ag and Au were successfully added to the wafer surface. Some of the metals were not reported (Sr, Mo, etc) due to space limitations
- All elemental extraction efficiencies were greater than 95 %

Preparation of Control Wafers

- An SC1 bath was formulated at the following composition levels; 4% NH_4OH, 16 % H_2O_2, 80 % DI H_2O
- SC1 dissolves the original SiO_2 layer where many of the metals are located from the manufacturing processes, and then reforms a new SiO_2 layer
- The bath was then spiked with a multi-element standard at 5, 50, and 500 ppt
- Wafers were submerged in the bath for 5 minutes with subsequent automatic wafer scanning and ICP-MS analysis
- Successive extractions were performed to asses extraction efficiency

Intentional Contamination - Correlation Study (1)



Agilent Technologies

Conclusions

- SME-ICP-MS offers a sensitive and accurate method for the characterization of trace metals on silicon wafer surfaces
- Silicon wafers can be prepared and analyzed in less than 20 minutes for the native oxide layer, and 30 minutes for the thermal oxide layer.
- This technique provides **real time** data for manufacturing quality assessments
- Fully investigated and developed methodologies

…continued

- Potential physical interferences associated with the analysis of the SME droplet matrix by ICP-MS can be virtually eliminated using the Agilent ShieldTorch System
- Pioneered by Agilent Technologies and its industry partners, SME-ICP-MS has become the industry standard technique for the characterization of trace metal contaminants on silicon wafer surfaces
- Agilent 7500s exceeds the National Technology Roadmap requirements for 450 mm wafers to the year 2009

References

Literature
Click on the titles to view the full article. You may need to complete a quick and easy registration step to access papers published in Semiconductor International.

- Characterization of Surface Metal Contamination on Silicon Wafers using Surface Metal Extraction Inductively Coupled Mass Spectrometry (SME-ICP-MS)
  Mike Radle and Tom Gluodenis
  Agilent Technologies Inc., USA
  Agilent 7500 Series ICP-MS application note 5988-4602EN
  September, 2001
- Characterizing Thermal Oxide Metals
  Huiling Lian, Beau Nicoley and Arnold J. Howard
  Intel Corp., Rio Rancho, N.M, USA
  Michael Radle
  Agilent Technologies, Bellevue, WA, USA
  Semiconductor International, July 1, 2001
- Using ICP-MS for in-line monitoring of metallics in silicon wafer cleaning baths
  Larry W. Shive, Kenneth Ruth, and Philip Schmidt
  MEMC Electronic Materials
  Micro Magazine
- Silicon Wafer Surface Metals Characterization by VPD-ICP-MS
  Mike Radle and Tom Gluodenis
  Agilent Technologies Inc., USA
  Agilent 4500 Series ICP-MS application note 5968-3236EN
  April, 2000
- Silicon Wafer Thermal Oxide Characterization by Surface Metals Extraction ICP-MS
  Huiling Lian, Beau Nicoley, and Arnold J. Howard
  Intel Corporation, New Mexico, USA
  Mike Radle
  Agilent Technologies Inc., USA

www.agilent.com/chem/semicon

Agilent Technologies