

# Characterization of Surface Metal Contamination on Silicon Wafers Using Surface Metal Extraction Inductively Coupled Plasma Mass Spectrometry (SME-ICP-MS)

Semiconductor

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## Abstract

**Surface Metal Extraction (SME) can be combined with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to characterize trace metal contaminants on a silicon wafer surface. Wafer sample preparation and analysis can be performed in less than 20 minutes thus allowing real time wafer production monitoring. Detection levels determined using this technique exceed the requirements for surface metallic contamination specifications for the year 2009.**

## Introduction

The current industry trend is toward the manufacture of semiconductor devices which exhibit faster operational speeds, smaller feature sizes, larger scales of integration, and lower manufacturing costs from yield enhancements and defect reduction. As device features continue to shrink to satisfy these goals, the need to characterize trace metal contamination on silicon wafer surfaces becomes more important. Contamination currently accounts for over 50% of the yield losses in semiconductor IC device manufacturing.

Surface contamination concentration techniques such as SME-ICP-MS have been used to determine the purity of both the native and thermal oxide layer on silicon wafers. This analysis can provide valuable information on the type, the source, and the levels of metallic contamination at almost every processing step in semiconductor manufacturing. Advantages of SME-ICP-MS include accurate analysis of up to 40 elements in a single droplet, excellent detection limits (part per trillion and sub part per trillion) and a 20-minute turn-around time for wafer preparation and analysis. These features of the SME-ICP-MS technique make it uniquely suited to perform real time wafer production monitoring.

The SME-ICP-MS application is particularly challenging due to the small sample volume, silicon rich matrix, and ultra-trace levels at which metal contaminants need to be measured. The instrument used in this application was an Agilent 7500s ICP-MS equipped with a MicroFlow nebulizer operating at 20 $\mu$ L/min. The exceptional sensitivity characteristic of the Agilent 7500s ICP-MS was



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further enhanced by operating the instrument in the soft extraction mode<sup>1,2</sup>. This mode of operation leverages the unique twin extraction lens design of the 7500s to apply a slight positive voltage to the first extraction lens. This counter-intuitive optimization procedure dramatically reduces the background across the entire mass range without any sacrifice in sensitivity. The result is a 10 to 100 fold increase in the signal-to-background ratio for most elements.

Potentially troublesome argon polyatomic ions were virtually eliminated using Agilent's exclusive ShieldTorch System (STS). Unlike traditional cool plasma conditions which require plasma powers of 500 – 550W, the Agilent 7500s is able to effectively eliminate argon based polyatomic interferences while operating at higher, more robust plasma conditions. This is primarily due to the 27.12 MHz generated, higher temperature plasma which promotes more efficient sample matrix dissociation and hence, higher sensitivity relative to cooler 40.68MHz generator designs. Also, the STS is highly efficient at reducing the plasma potential to approximately 1 eV – significantly lower than with non-shield plasma locking devices. This leads to better ion focusing and more efficient interference removal thereby alleviating the need for sample pretreatment or complex scanning reaction/collision cell technologies.

The use of a MicroFlow nebulizer, Peltier cooled spray chamber, wide bore torch injector, and highly efficient 27MHz plasma generator ensured complete ionization of the sample matrix thereby eliminating concerns regarding analytical stability. In addition, the flat mass response curve of the robust Omega II ion lens system resulted in efficient transmission of the analyte ions to the quadrupole mass filter with the same high sensitivity across the entire mass range. Combined, these design features minimized ion suppression resulting from the silicon rich sample matrix thereby eliminating the need for MSA (method of standard additions), matrix matching, or internal standards which could potentially contaminate the samples undergoing ultra-trace analysis.

## METHODOLOGY

### Sample Preparation

The silicon wafer was placed in a cleaned PTFE chamber and exposed to HF to dissolve the SiO<sub>2</sub> surface layer. The wafer surface was then scanned with a 250 uL extraction droplet. This can be done manually or with an automated wafer scanner. The extraction droplet collects the

contents of the dissolved silicon layer as it is moved across the wafer surface. The extraction droplet was then pipetted from the wafer surface, deposited into an autosampler, and analyzed by ICP-MS. The calibration blank and standards used in this study were prepared at 0, 100, 250 and 500 ppt in 5% HF and 6% H<sub>2</sub>O<sub>2</sub>.

High purity silicon was cleaned in HF and peroxide then dissolved in 10g HF (49%), 18g H<sub>2</sub>O<sub>2</sub> (30%), and 72g of UPW. Note that some small degree of metals contamination may be present from the silicon, which has gone through all the manufacturing steps from crystal growth through wafer thermal processing. This final solution, containing 0.59ppm Si (verified independently) was used as a synthetic SME matrix to determine spike recoveries. A synthetic matrix was used rather than an actual SME droplet due to the difficulties associated with spiking into a small sample volume without diluting the sample matrix. This method of sample preparation offers a much more rigorous test of instrument performance than simply spiking a standard solution of Si.

### ICP-MS Analysis

An Agilent 7500s ICP-MS equipped with the ShieldTorch System and a Micro Flow nebulizer was used for this analysis. The sample was self-aspirated at an uptake rate of 20 uL/min. Instrument operating conditions are given in Table 1.

**Table 1. ICP-MS operating conditions**

Parameter	STS Conditions	Soft Extraction Conditions
RF Power	800W	1540 W
Sampling Depth	14.2 mm	9.2 mm
Carrier Gas Flow	0.8 L	1 L
Makeup Gas Flow	0.75 L	0 L
Extraction Lens 1	- 152 V	+ 4 V
Extraction Lens 2	- 22 V	- 46 V

Switching between STS conditions and soft extraction mode is completely automated using Agilent's Multi-tune software. Multi-tune allows complete data collection in a single acquisition, with a single visit to the sample vial, thereby saving time and reducing the potential for sample contamination. In addition, all resulting data is compiled in a single report. Stabilization time in switching between operating modes is minimal with only 20 seconds required when switching from soft extraction to STS conditions. The stability of switching between operating modes over prolonged periods has been previously demonstrated to be

stable to approximately 3% RSD over an 8 hour period of time<sup>3</sup>.

Three sigma detection limits were determined using the constructed calibration curve. A synthetic SME sample matrix containing 5% HF, 6% H<sub>2</sub>O<sub>2</sub>, and 0.59 ppm silicon (typical of native oxide layers – the most common application of SME) was analyzed to evaluate the magnitude of any physical or spectral interferences arising from the matrix. The synthetic SME matrix was then spiked with a multielement standard at a concentration of 10ppt. The spiked and unspiked matrix droplets were analyzed and spike recoveries calculated.

The results shown in Table 2 show detection limits for a standard suite of semiconductor elements both in the calibration matrix and in the simulated SME matrix. Note the exceptional performance even for more difficult elements such as Ca, K, and Fe. A small trace of Co was observed in the calibration matrix and this has biased the result for this particular element high; however, at 1.38ppt, this remains well within industry guidelines. All other elements, including Co in the high silicon matrix, return sub-ppt detection limits. Also note that these results were obtained with a 20 uL/min sample uptake rate and that the detection would be improved even further if the more common 100 uL/min MicroFlow Nebulizer were used. Representative calibration curves are given in Figure 1.

## Results and Discussion

**Table 2. Detection limits (parts per trillion) in the SME matrix**

Element	Mass	No Silicon 7500 DL (ppt)	0.59 ppm Silicon 7500 DL (ppt)	450 mm Wafer DL (atoms/cm <sup>2</sup> )	NTRS 2009 Requirements
Li	7	0.03	0.02	4.1 E5	<1.0 E11
Na	23	0.20	0.27	8.2 E5	<2.5 E9
Mg	24	0.17	1.00	6.6 E5	<1.0 E11
Al	27	0.05	0.16	1.8 E5	<1.0 E11
K	39	0.57	3.3	1.4 E6	<2.5 E9
Ca	40	0.26	0.97	6.1 E5	<2.5 E9
Cr	52	0.04	0.81	7.3 E4	<2.5 E9
Mn	55	0.02	0.18	3.4 E4	<2.5 E9
Fe	56	0.3	0.95	5.1 E4	<2.5 E9
Co	59	1.4	0.58	2.2 E6	<2.5 E9
Ni	60	0.74	1.0	1.2 E6	<2.5 E9
Cu	63	0.25	0.14	3.7 E5	<2.5 E9
Zn	68	0.86	3.0	1.2 E6	<2.5 E9
Zr	90	0.22	0.27	2.3 E5	NA
Sn	118	0.29	0.48	2.3 E5	NA
Ta	181	0.03	0.04	1.6 E4	NA
Au	197	0.09	0.12	4.3 E4	NA
Pb	208	0.02	0.09	9.1 E3	NA

A comparison of the detection limits measured in the calibration matrix with that obtained in the SME synthetic matrix exhibits no significant differences. These results highlight the effectiveness of the ShieldTorch interface in effectively removing matrix-based polyatomic interferences while efficiently ionizing elements with high ionization potentials, such as Zn, in the high silicon matrix. Further evidence of the

effectiveness of the ShieldTorch System in eliminating matrix based interferences without loss of sensitivity has been documented previously by Howard et. al in which the authors demonstrated quantitative recovery of a 495ppt multielement spike solution in SME matrices containing 100, 250, 500, and 1000 ppm silicon<sup>4</sup>.

If there were a loss of plasma ionization energy due to the SME sample matrix, poor spike recoveries would be expected. Elements with a high ionization energy, such as Zn, would show the greatest signal loss and the lowest spike recovery. The results given in Table 3 demonstrate excellent spike recoveries for all elements, therefore indicating negligible plasma ionization suppression from

the SME sample matrix. The quantitative recovery also indicates the absence of any nebulization or transport interferences. Note: all recoveries were determined without the use of an internal standard therefore simplifying sample preparation and eliminating a potential source of contamination.

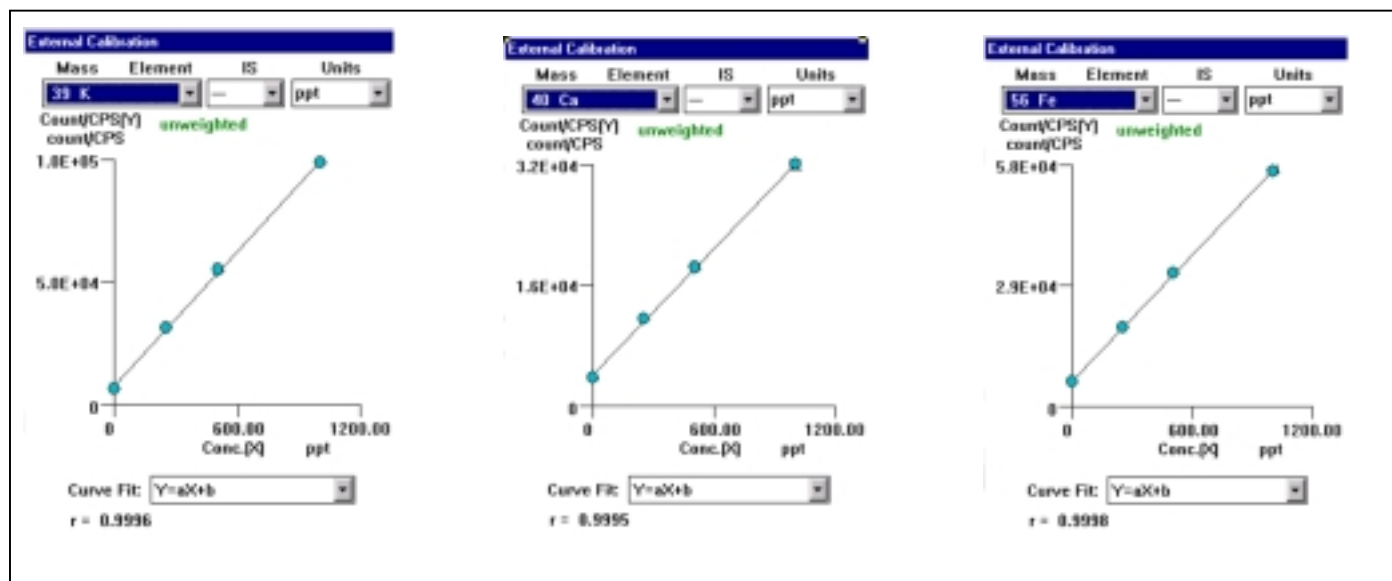


Figure 1. Representative calibration curves for K, Ca and Fe at 0, 250, 500 and 1000 ppt

Table 3. Spike recoveries in the synthetic extraction droplet

Element	Mass	Conc (ppt)	% Recovery	Element	Mass	Conc (ppt)	% Recovery
Li	7	9.8	98	Cu	63	9.9	99
Be	9	11.0	110	Zn	68	11.5	115
B	11	9.5	95	Ga	69	9.9	99
Na	23	9.5	95	Ge	70	10.6	106
Mg	24	9.8	98	As	75	9.1	91
Al	27	10.3	103	Sr	88	10.2	102
K	39	9.9	99	Zr	90	10.3	103
Ca	40	9.6	96	Cd	111	9.5	95
Ti	47	10.8	108	Sn	118	10.0	100
V	51	9.9	99	Sb	121	9.6	96
Cr	53	9.4	94	Tl	205	10.0	100
Mn	55	10.0	100	Pb	208	10.0	100
Co	59	10.0	100	Bi	209	9.9	99
Ni	60	10.1	101				

The detection limits given in Table 2 were used to calculate the corresponding wafer detection limits (atoms/cm<sup>2</sup>) for surface metals on a 450-mm wafer. The current performance of the SME-ICP-MS technique described exceeds the projected requirements for 450-mm wafer surface contamination for the year 2009.

## Conclusions

The SME-ICP-MS technique 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 providing real time data for manufacturing quality assessments. Potential physical interferences associated with the analysis of the SME droplet matrix by ICP-MS can be virtually eliminated using STS conditions. This combined with the soft extraction mode of operation results in detection capability that is orders of magnitude below what the National Technology Roadmap will require for 450mm wafers to the year 2009.

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