

Silicon Wafer Surface Metals Characterization by Vapor Phase Decomposition Inductively Coupled Plasma Mass Spectrometry (VPD-ICP-MS)

Application Note

Semiconductor

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Abstract

Vapor phase decomposition (VPD) 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.



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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.

The VPD-ICP-MS analytical technique was developed for the measurement of trace metals in the native oxide layer and on the surface of 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 VPD-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 30 minute turn-around time for wafer VPD preparation and analysis. In addition, improved accuracy and precision can be realized through the use of matrix matched standards.

These features of the VPD-ICP-MS technique make it uniquely suited to perform real time wafer production monitoring.

VPD Sample Preparation and Analysis

The silicon wafer is placed in a VPD chamber, and exposed to HF vapor for 10 minutes to dissolve the SiO₂ surface layer. The wafer surface is then scanned with a 250- μ L extraction droplet. This can be done manually or with an automated wafer scanner. The extraction droplet picks up the contents of the dissolved silicon layer as it is moved across the wafer surface. The extraction droplet is then pipetted from the wafer surface and analyzed by ICP-MS

A Agilent Technologies 4500 ICP-MS was used for the analysis of the VPD droplet. The instrument was equipped with a cross flow nebulizer specifically designed for use with limited sample volumes. The sample was self-aspirated at an uptake rate of 100 μ L/min. Platinum cones were used for the analysis. Instrument operating conditions are given in Table 1.

Parameter	Value
RF power	930 Watts
Carrier gas	1.0 L/min
Blend Gas	0.55 L/min
Sampling Depth	16 mm
Spray chamber temperature	2 °C
Lens voltage	optimized for cool plasma analysis
Peak Pattern	3 points/peak
Integration Time	1 sec/point

Table 1.
ICP-MS operating conditions

Matrix Effects and Potential Interferences

The analysis of critical elements in semiconductor process chemicals has typically required the use of low power cool plasma conditions to minimize argon molecular interferences. In this technique, the instrument is operated at a plasma power of 500-700W with re-optimization of nebulizer gas flow, lens voltages, and plasma sampling depth. Although operation of the ICP-MS under these conditions will reduce argon-based interferences, it also significantly reduces the energy of the plasma. Consequently, there is a dramatic loss of sensitivity for elements having high ionization potentials and significant plasma loading effects associated with heavy matrices. The VPD-ICP-MS results reported in this work were performed using a plasma power of 930 W. The higher plasma power compensates for plasma loading caused by the dissolved solids and reagents in the VPD sample matrix while at the same time reducing argon based interferences on critical elements such as Fe and Ca.

Physical interferences associated with the chemical composition of the VPD extraction matrix can also be compensated for, by using matrix matched calibration standards. The calibration blank and standards employed in this study were prepared at 0, 100, 250 and 500 ppt in a 5 % HF, 6 % H₂O₂ matrix. Typical calibration curves are given in Figure 1.

Effectiveness of Cool plasma Analysis for Interference Reduction

The reduction of interferences resulting from sample nebulization, sample transport, and plasma loading were evaluated. Recoveries were determined for a synthetic VPD matrix spike. A synthetic matrix was utilized rather than an actual VPD droplet

because of the difficulties associated with spiking into a small sample volume without dilution of the matrix. Silicon was analyzed in a number of actual VPD samples to determine the amount of silicon the synthetic matrix should contain. The average silicon concentration determined was 330 ppb. The synthetic matrix was formulated at 1000 ppb silicon to approximate a worst case scenario.

The synthetic VPD matrix was then spiked with a multielement standard at a concentration of 213 ppt. The spiked and unspiked droplets were analyzed and the spike recoveries calculated. If there was a loss of plasma ionization efficiency due to the VPD 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 2 demonstrate excellent spike recoveries for all elements, therefore indicating negligible plasma ionization suppression from the VPD sample matrix. The quantitative recovery of the sample spike also indicates the absence of any nebulization or transport interferences.

ICP-MS Detection Limits in the VPD Chemical Matrix

Table 3 lists the detection limits (ppt) determined in the VPD extraction droplet chemical matrix. The first detection limit is a 3-sigma calculation using standard and blank data in the given calculation.

The second detection limit is determined from the upper 95 % confidence level error bar derived from individual element calibration curves. The derivation of this detection limit is described in SEMI C10-94, "Guide for Determination of Method Detection Limits for Trace Metal Analysis by Plasma Spectroscopy."¹ These values were used to calculate the corresponding wafer detection limits (atoms/cm²) for surface metals on 150-mm, 200-mm and 300-mm wafers. Also listed in Table 3 are the National Technology Roadmap for Semiconductors (NTRS) 300-mm wafer surface

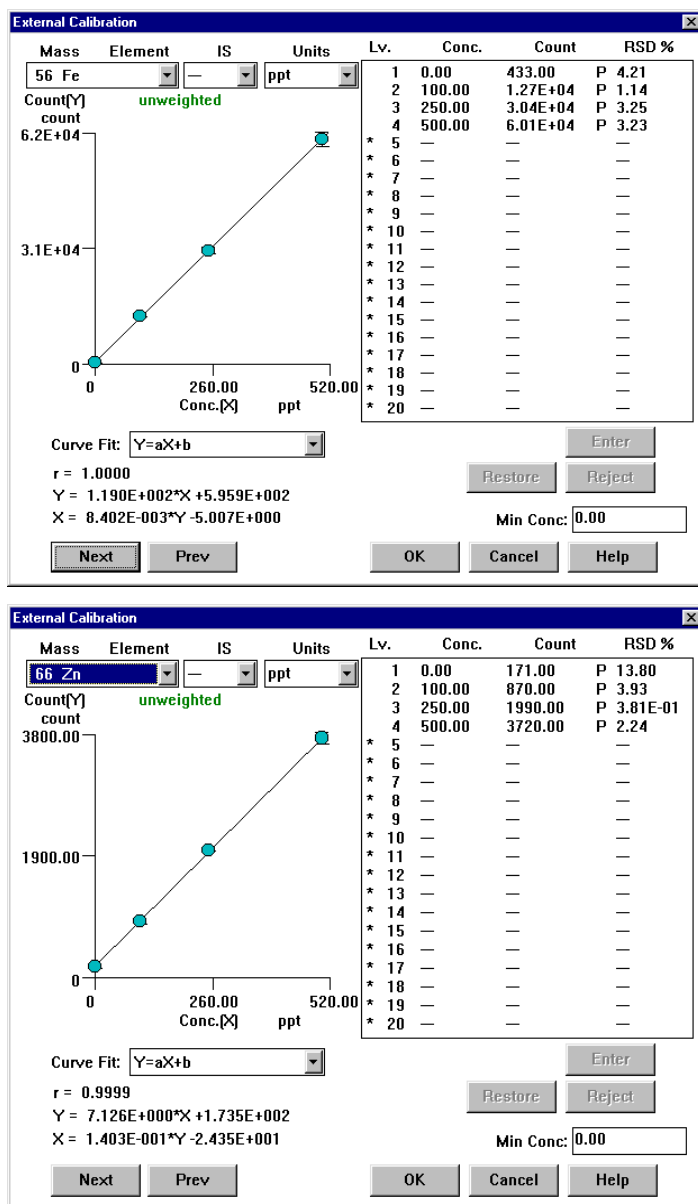


Figure 1. Typical Calibration Curves Using Matrix Matched Standards.

metal requirements for the year 1999². The VPD process combined with metals determination using the 4500 ICP-MS currently exceeds all of the required levels of detection for surface metals contaminants by at least a factor of 10.

NTRS Material Requirements for Year 2009²

The projected requirements for critical surface metal levels (atoms/cm²) on a 450-mm wafer in the year 2009 are listed in Table 4. Also listed are the current 4500 ICP-MS wafer detection limits calculated for a 450-mm wafer. Again, the current performance of the VPD-ICP-MS technique described, exceeds the projected requirements for 450mm wafer surface contamination for the year 2009.

Conclusion

The VPD-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 30 minutes providing real time data for manufacturing quality assessment. Potential physical interferences associated with analysis of the VPD droplet matrix by ICP-MS can be virtually eliminated, by matrix matching of the calibration standards and through judicious selection of instrument operating conditions. Operation of the ICP-MS with relatively high-power cool plasma conditions provides the higher plasma temperature required for the analysis of high-matrix samples, as well as reduction of argon based molecular interferences. Optimum performance at these plasma powers

Element	Mass	1st Ionization Potential (eV)	Spike Concentration (ppt)	Recovered Concentration (ppt)	% Recovery
Li	7	5.39	213	217	102
Na	23	5.13	213	225	106
Mg	24	7.64	213	211	99
Al	27	5.98	213	211	99
K	39	4.33	213	222	104
Ca	40	6.11	213	185	87
Cr	52	6.76	213	219	103
Mn	55	7.43	213	209	98
Fe	56	7.87	213	224	105
Ni	60	7.63	213	211	99
Co	59	7.86	213	217	102
Cu	65	7.72	213	221	104
Zn	68	9.93	213	213	100
Ag	107	7.57	213	213	100

Table 2.
Spike recovery data for elements in the simulated VPD sample matrix.

$$\text{Detection Limit (ppt)} = \frac{(3 \times \text{blank std dev})}{(\text{standard counts} - \text{blank counts})} \times (\text{concentration of standard in ppt})$$

Detection Limit Calculation

Element	3 Sigma DL (ppt)	SEMI Method (ppt)	150-mm wafer, 250 µl drop, (atoms/cm ²)	200-mm wafer, 250 µl drop, (atoms/cm ²)	300-mm wafer, 250 µl drop, (atoms/cm ²)	NTRS 300 mm Wafer Requirements, 1999
Li	0.03	15	1.9 E9	1.1 E9	4.6 E8	< 1.0 E11
Na	0.3	17	6.3 E8	3.5 E8	1.6 E8	< 1.3 E10
Mg	3	20	7.2 E8	4.1 E8	1.8 E8	< 1.0 E11
Al	3	19	5.9 E8	3.3 E8	1.5 E8	< 1.0 E11
K	18	25	5.4 E8	3.0 E8	1.4 E8	< 1.3 E10
Ca	20	25	5.3 E8	3.0 E8	1.3 E8	< 1.3 E10
Cr	4	24	3.9 E8	2.2 E8	9.8 E7	< 1.3 E10
Mn	0.8	16	2.6 E8	1.4 E8	6.2 E7	< 1.3 E10
Fe	17	21	3.2 E8	1.6 E8	8.0 E7	< 1.3 E10
Co	10	25	3.6 E8	2.0 E8	9.0 E7	< 1.3 E10
Ni	5	23	3.4 E8	1.9 E8	8.2 E7	< 1.3 E10
Cu	3	16	2.2 E8	1.2 E8	5.4 E7	< 1.3 E10
Zn	7	33	4.2 E8	2.4 E8	1.1 E7	< 1.0 E11

Table 2.
Spike recovery data for elements in the simulated VPD sample matrix.

can only be achieved with optimization of plasma sampling depth. All of the critical surface metal contaminants on silicon

wafer surfaces can be determined under a single set of cool plasma operating conditions. Detection limits determined using VPD and

Element	4500 ICP-MS LOD, (atoms/cm ²)	NTRS, Year 2009 Wafer Requirements
Li 7	2.0 E8	< 1.0 E11
Na 23	7.0 E7	< 2.5 E9
Mg 24	8.0 E7	< 1.0 E 11
Al 27	6.7 E7	< 1.0 E 11
K 39	6.1 E7	< 2.5 E9
Ca 40	6.0 E7	< 2.5 E9
Cr 52	4.4 E7	< 2.5 E9
Mn 55	2.8 E7	< 2.5 E9
Fe 56	3.6 E7	< 2.5 E9
Co 59	4.0 E7	< 2.5 E9
Ni 60	3.6 E7	< 2.5 E9
Cu 65	2.4 E7	< 2.5 E9
Zn 68	4.7 E7	< 1.0 E 11

Table 4.
4500 ICP-MS Wafer Detection Limits (450-mm Wafer, 250 μ L Drop)

the 4500 ICP-MS are orders of magnitude below what the National Technology Roadmap will require beyond the year 2000 for both 300-mm and 450-mm wafers.

References

- (1) SEMI C10-94 Guide for Determination of Method Detection Limits for Trace Metal Analysis by Plasma Spectroscopy.
- (2) The National Technology Roadmap for Semiconductors, San Jose, Semiconductor Industry Association, 1994.

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