

Characterization of Trace Impurities in Silicon Wafers by High Sensitivity Reaction Cell ICP-MS

Application

Semiconductor

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Abstract

A newly designed, high-sensitivity reaction cell inductively coupled plasma mass spectrometer (ICP-MS) was used to determine trace metals in the presence of a high concentration of silicon (2000 ppm). A number of silicon-based interferences prevent straightforward analysis of titanium, nickel, copper, and zinc by conventional ICP-MS so the test also served to evaluate the magnitude of any physical or spectral interferences arising from the matrix. The 7500cs ICP-MS incorporates an Octopole Reaction System for interference removal, allowing the analysis of these elements directly at the analyte mass. Detection levels for all Semiconductor Equipment and Materials International (SEMI) required elements determined using this technique are in the range 0.20–40 ppt.

Introduction

Semiconductor manufacturers are constantly striving to improve devices and lower manufacturing costs. Device improvements demand increased miniaturization, faster operational speeds, and greater integration. Lowering manufacturing costs requires higher yields and decreased device defects. As device features are minimized to meet these goals, the need to characterize trace metal contamination in silicon wafers at lower concentrations becomes more important. Various surface contamination concentration sampling techniques are used to determine the purity of both the native and thermal oxide layer on silicon wafers, including surface metal extraction (SME) and liquid drop decomposition (LDD). The silicon concentration of a sample solution obtained from the naturally oxidized layer is less than 10 ppm, while it is up to 2000 ppm for the thermally oxidized layer. Sample solutions for bulk silicon wafer analysis contain silicon up to the 2% level. Applications relating to silicon wafer analysis are particularly challenging due to the small sample volumes, for example a 200–250 μL sample volume is typical of the SME technique; the silicon-rich matrix and aggressive reagents used to prepare silicon wafer samples for



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analysis; and the ultratrace levels at which metal contaminants need to be measured. The instrument used in this application was an Agilent 7500cs ICP-MS equipped with a low flow nebulizer. The use of a MicroFlow nebulizer (MFN-100), Peltier cooled spray chamber, wide diameter torch injector, and highly efficient 27 MHz plasma generator operating at 1600 W (normal power) ensured complete ionization of the sample matrix, thereby eliminating concerns regarding analytical stability.

High Silicon Matrix - Interference Removal

Polyatomic overlaps on some semiconductor-critical elements present specific analytical problems for conventional quadrupole ICP-MS for many semiconductor applications. Plasma based interferences Ar, ArH, and ArO limit the determination of Ca, K, and Fe respectively, while silicon-based interferences (shown in Table 1) interfere with important elements such as Ti, Ni, Cu, and Zn. With the 7500cs reaction cell ICP-MS, analysts can attenuate interferences using a controlled environment within the Octopole Reaction System (ORS) cell, which is pressurized with the simple cell gases hydrogen (reaction mode) and helium (collision mode).

Table 1. Silicon-Based Polyatomic Interferences on Ti, Ni, Cu, and Zn

Polyatomic ions	Mass	Analyte
^{30}SiO , $^{29}\text{SiOH}$	46	Ti
^{28}SiF , $^{30}\text{SiOH}$	47	Ti
^{29}SiF , $^{28}\text{SiFH}$	48	Ti
^{30}SiF , $^{29}\text{SiFH}$	49	Ti
$^{28}\text{SiO}_2$	60	Ni
$^{28}\text{SiOF}$, $^{30}\text{SiO}_2\text{H}$	63	Cu
$^{29}\text{SiOF}$, $^{28}\text{SiOFH}$	64	Zn
$^{30}\text{SiOF}$, $^{29}\text{SiOFH}$	65	Cu
$^{28}\text{SiF}_2$, $^{30}\text{SiOFH}$	66	Zn
$^{30}\text{SiF}_2$, $^{29}\text{SiF}_2\text{H}$	68	Zn

Methodology

Sample Preparation

Pieces of silicon wafers were soaked in 1:3 HF solution for 10 minutes to remove any surface deposits. The wafer surfaces were then rinsed and dried in a stream of argon gas. Bulk silicon pieces (2 g) were digested in high-purity grade HF (25 g) (Tama Pure Chemicals, Japan) and HNO_3 (15 g) in a sealed vessel, which was heated to 60 °C on a hot plate. Vigorous shaking was necessary to dissolve any by-products, for example, ammonium fluorosilicate. On cooling, ultrapure water was added to make up a 2% silicon solution, and these were further diluted by a factor of 10 using 3.8% HF and 6.8% HNO_3 to produce a final concentration of 0.2% (2000 ppm).

ICP-MS Analysis

An Agilent 7500cs ICP-MS equipped with an ORS, ShieldTorch System (STS) and an MFN-100 was used for this analysis. The sample was aspirated at an uptake rate of 68 $\mu\text{L}/\text{min}$. A platinum 2.0-mm injector torch, perfluoroalkoxyalkane (PFA) spray chamber and PFA endcap were also used. The 7500cs is fitted with a platinum interface as standard. Instrument operating conditions are given in Table 2.

Table 2. ICP-MS Operating Conditions

Parameter	ICP-MS Conditions
RF Power	1600 W
Sampling depth	8 mm
Carrier gas flow	0.45 mL/min
Makeup gas flow	0.68 mL/min
Extraction lens 1	-152 V
Extraction lens 2	-22 V

Method of Quantification

Calibrations were performed using matrix-matched 2000 ppm silicon standards. One of the digested Si samples was spiked to final concentrations of 0, 20, 60, and 100 ppt with multi-element standards to create an external calibration. All other Si sample concentrations were determined against this external calibration and were corrected to account for the dilution factors. No internal standards were added to avoid the risk of contamination. The external calibration avoided the need for time consuming standard additions, which require the need to spike every sample.

The effectiveness of the external, matrix-matched calibration was gauged by spiking samples with a multi-element standard at a concentration of 50 ppt (ng/L) and calculating recoveries. Figure 1 illustrates a representative calibration curve, in this case Cu in the matrix matched solution.

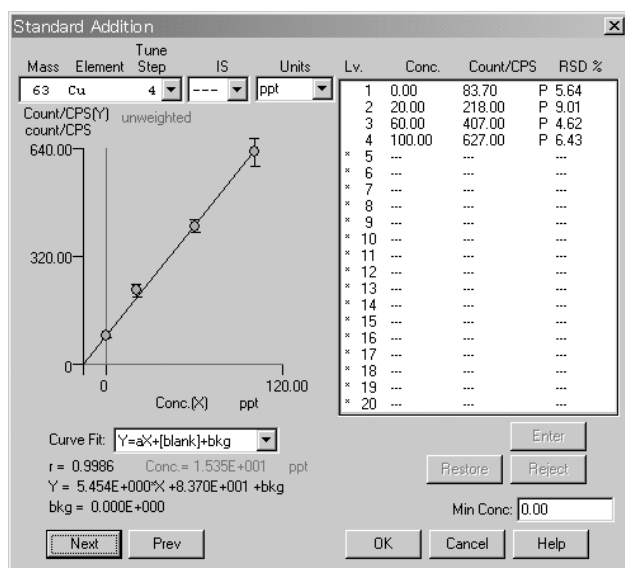


Figure 1. Copper calibration curve in 2000 ppm silicon solution.

Results and Discussion

Detection limits (DL) and background equivalent concentrations (BEC) for a full suite of semiconductor elements in the 2000 ppm silicon sample are summarized in Table 3. As the data in the table demonstrates, all elements in the high silicon matrix return DL and BEC at ppt levels, even for the more difficult elements K, Ca, Ti, Fe, Ni, Cu, and Zn. These results highlight the effectiveness of the ORS cell for removing plasma and matrix-based polyatomic interferences in the high silicon matrix.

Table 3. DL (3 sigma), BEC and Spike Recoveries of SEMI Specified Elements in 2000 ppm Silicon Sample

Element (mass)	Plasma power (W)	H ₂ Gas flow (mL/min)	He Gas flow (mL/min)	DL 3 sigma, n = 10 (ppt)	BEC (ppt)	Spike recovery (%) 50 ppt spike
Li (7)	1600	-	-	0.64	1.2	81
Be (9)	1600	-	-	1.1	1.4	82
B (11)	1600	-	-	6.6	22	79
Na (23)	1600	5.0	-	16	18	95
Mg (24)	1600	-	-	0.68	2.9	83
Al (27)	1600	5.0	-	6.9	7.7	113
K (39)	1600	5.0	-	12	36	79
Ca (40)	1600	5.0	-	9.8	45	91
Ti (48)	1600	-	5.0	40	76	94
V (51)	1600	-	5.0	0.72	0.17	93
Cr (52)	1600	5.0	-	7.8	7.5	97
Mn (55)	1600	5.0	-	1.3	2.2	91
Fe (56)	1600	5.0	-	2.7	31	87
Co (59)	1600	-	5.0	1.6	2.6	98
Ni (60)	1600	-	5.0	6.8	6.9	94
Cu (63)	1600	-	5.0	2.6	15	95
Zn (64)	1600	-	5.0	11	14	94
Ga (71)	1600	-	5.0	15	51	95
Ge (72)	1600	-	5.0	8.1	3.3	90
As (75)	1600	-	5.0	18	19	94
Sr (88)	1600	-	-	0.91	1.6	82
Zr (90)	1600	-	-	1.5	2.3	84
Nb (93)	1600	-	-	0.31	0.30	83
Mo (95)	1600	-	-	2.1	2.1	85
Ag (107)	1600	-	-	2.7	4.5	80
Cd (111)	1600	-	-	1.4	1.5	88
Sn (118)	1600	-	-	0.84	2.8	85
Sb (121)	1600	-	-	0.29	0.80	84
Ba (137)	1600	-	-	1.3	0.90	85
Ta (181)	1600	-	-	0.18	0.17	85
Au (197)	1600	-	-	2.5	2.0	86
Tl (205)	1600	-	-	0.40	0.23	82
Pb (208)	1600	-	-	0.81	1.2	85
Bi (209)	1600	-	-	0.81	1.3	84
Th (232)	1600	-	-	0.20	0.19	80
U (238)	1600	-	-	0.28	0.18	81

The 50-ppt spike recoveries for all elements are in the SEMI specified range of 75%-125%. 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.

A short-term stability study was performed by adding a 100-ppt standard into a 1000-ppm silicon solution and analyzing the spiked sample over a 2-hour period. Instrument stability over this period was excellent with %RSD values typically 5%. A stability plot of representative elements is shown in Figure 2.

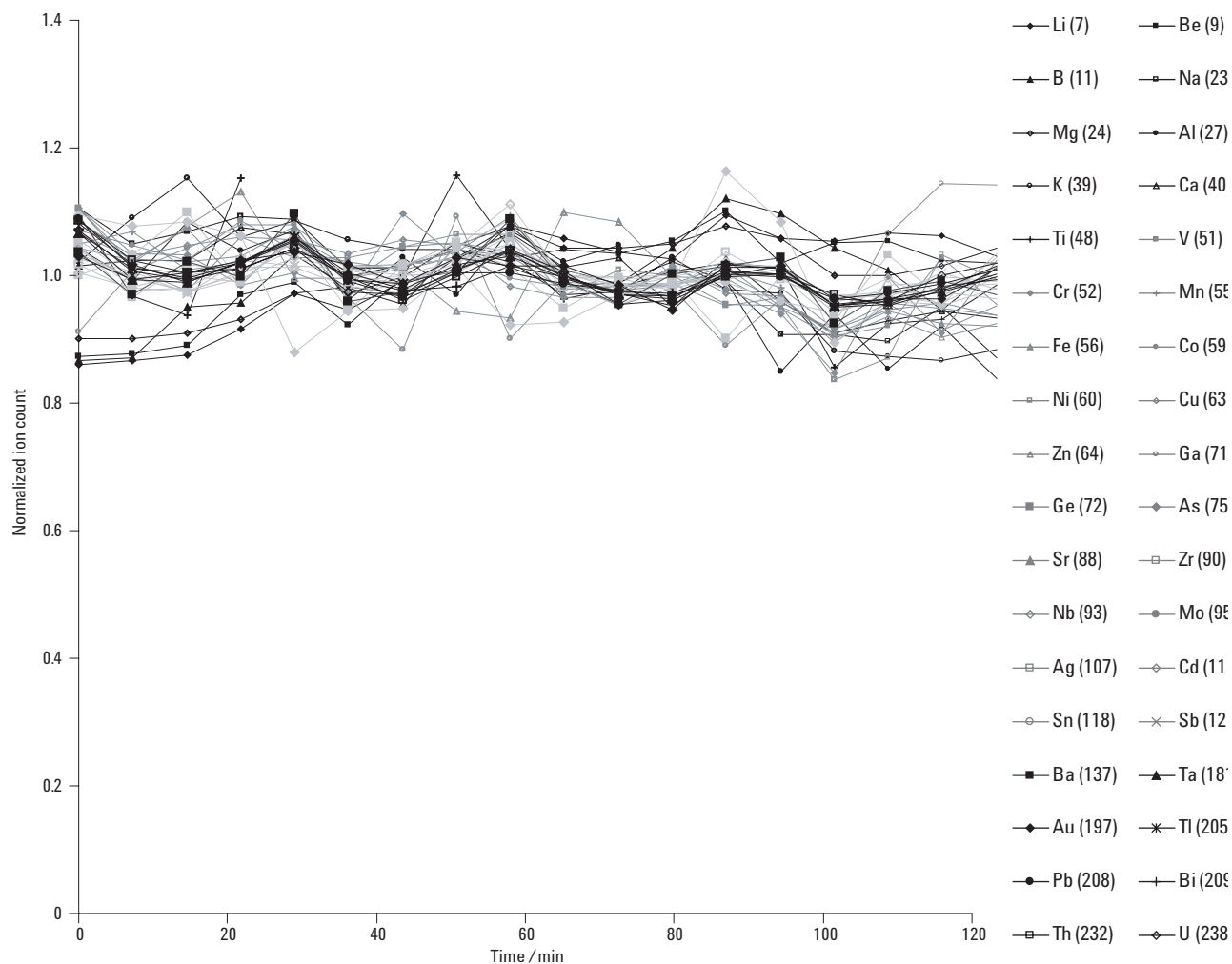


Figure 2. Analysis of 100-ppt multi-element standard spiked into 1000-ppm silicon solution measured repeatedly over a 2-hour period. Analysis time per sample was 340 s including 60 s sample uptake time and three replicate measurements.

Conclusions

The 7500cs ORS with a MicroFlow nebulizer (MFN-100) was used to determine 36 elements in a 2000 ppm Si matrix sample, with a full analysis taking only about 5 minutes for a sample volume of about 350 μ L. A simple sample preparation method is described, which is applicable to the analysis of bulk silicon wafer samples. All analytes were measured directly on mass, in a single analytical run with automatic switching of operating parameters (all data was acquired under normal plasma operating conditions, that is, 1600 W RF forward power) and with the results being combined automatically into a single report. The results highlight the effectiveness of the ORS for removing plasma and matrix-based polyatomic interferences on K, Ca, Fe, Ti, Ni, Cu, and Zn in the presence of a high concentration of silicon. All potential interferences are attenuated using the ORS with simple gases H₂ or He, and the analysis is fast and robust. The 50 ppt spike recovery data demonstrate the effectiveness of operating at high RF power with negligible plasma ionization suppression from the high silicon sample matrix. The quantitative recovery also indicates the absence of any nebulization or transport interferences.

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