

# Analysis of Silicon Wafers Using the ELAN DRC ICP-MS

## Introduction

The control of impurity levels in silicon-based semiconductor devices is critical because even ultratrace amounts of impurities, including alkali and alkali-earth elements and transition metals, can cause defects such as voltage breakdown or high dark current. For quality control purposes, there are two types of silicon that are routinely analyzed, bulk silicon and the surface of silicon wafers. Bulk silicon analysis can be performed by totally digesting the silicon using a very aggressive acid. Vapor phase decomposition is the most common method used for the analysis of silicon wafers. For bulk silicon analysis, sample volume is not an issue; however, small sample volumes are desirable in order to minimize time-consuming sample preparation. For the analysis of silicon wafers, impurities on the wafer surface are collected using a very small amount of acid deposited on the surface as a droplet. This results in a typical sample volume of around 200  $\mu\text{L}$ . Both types of silicon analysis require the ability to handle small sample volumes and high silicon matrices, as well as a hydrofluoric (HF) acid-resistant sample introduction system. Since a typical analysis may take 2-3 minutes per sample, low-flow nebulizers with sample uptake rates from 40-100  $\mu\text{L}/\text{min}$  are routinely used.

Adding to the complexity of the analysis for silicon impurities is the fact that many of the critical analytes are difficult to analyze by Inductively Coupled Plasma Mass

Spectrometry (ICP-MS) because they suffer from plasma-based molecular and isobaric interferences such as  $\text{ArO}$ ,  $\text{ArH}$ , and  $\text{Ar}$ . Cool plasma has previously been used to reduce these interferences. However, the amount and type of sample introduced into the plasma plays an important role in the performance achievable using cool plasma conditions. When low-flow nebulizers are used with cool plasma, the low sample flow rate does not cool the plasma enough to eliminate the  $\text{Ar}$  and  $\text{ArH}$  interferences, resulting in higher backgrounds for  $\text{Ca}$  and  $\text{K}$ , respectively. In addition, cool plasma suffers from severe matrix suppression with high matrix samples because the plasma is insufficient to break up the sample matrix. As a result, the method of standard additions (MSA) calibration is often used. MSA has many disadvantages, such as being a time-consuming procedure, requiring multiple sample aliquots, and acid blank contamination levels cannot be subtracted. This combination of factors makes the analysis of high silicon samples with cool plasma difficult due to matrix effects and the inability of cool plasma to reach the necessary detection limits.

The ELAN<sup>®</sup> DRC<sup>™</sup> (Dynamic Reaction Cell<sup>™</sup>) ICP-MS does not need to use cool plasma because it uses a technique called chemical resolution to remove the interferences. By providing a low flow of the proper reaction gas into the patented Dynamic Reaction Cell and using the unique Dynamic

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Bandpass Tuning (DBT) feature, interferences can be chemically scrubbed out of the ion beam before they enter the analyzer quadrupole of the mass spectrometer. Another advantage of the ELAN DRC is that it always operates under robust hot plasma conditions, effectively decomposing the sample matrix and eliminating the need for matrix-matched standards or MSA. The ELAN DRC also has the ability to combine elements run in DRC mode (with reaction gas) with elements run in standard mode (without reaction gas) in a single analytical run, eliminating the need for running the sample twice or under two different plasma conditions. The results obtained by both modes (DRC and standard) are combined by the instrument software and printed out in one report. It is also possible to determine an element in both DRC mode and standard mode in the same run and directly compare the results. This application note will show how the ELAN DRC eliminates interferences for the analysis of small volume silicon-matrix samples using a low-flow nebulizer for the analysis of impurities in silicon.

## Experimental

**Sample Preparation:** A bulk silicon sample (Hemlock Semiconductor Corporation, Hemlock, MI, USA) was digested with a small amount of concentrated high-purity HF and HNO<sub>3</sub> acids. Several aliquots of the digested sample were then diluted to obtain samples containing 100, 500, 1000, 2000, and 5000 ppm of Si. The final acid concentration in each sample was adjusted to contain 4% HF and 6% HNO<sub>3</sub>. Two samples were prepared for each Si concentration and one of each pair was spiked with a standard solution (PerkinElmer Pure™, Norwalk, CT, USA) in order to perform a spike recovery test. Calibration solutions in 4% HF and 6% HNO<sub>3</sub> (Tama Pure Chemicals Co., Tokyo, Japan) were prepared from multi-element solutions (PerkinElmer Pure, Norwalk, CT, USA).

**Instrument Conditions:** The instrument used was the ELAN DRC ICP-MS. The instrument operating conditions and sample introduction system used for this experiment are shown in Table I.

The elements determined and the instrument mode used are shown in Table II.

## Results

**Stability:** Since silicon is a refractory element, it tends to form oxides in the plasma, particularly when cool plasma conditions are used. These silicon oxides deposit on the surface of the interface cones, causing significant signal drift. The ability of the ELAN DRC to use hot plasma conditions for all analyses should greatly reduce this signal drift. In order to show the benefit of using the more robust hot plasma conditions, a 500-ppm silicon sample spiked with a 500-ppm multi-element standard solution was continuously introduced to

the ELAN DRC for two hours, while readings were taken every 10 minutes. As shown in Figure 1, the magnesium signal under the standard mode and the potassium, calcium, and iron signals under DRC mode were very stable even during constant nebulization of the sample solution. The relative standard deviation (RSD) for all readings for each element is shown in parentheses in the Figure 1 legend next to each analyte.

**Spike Recovery:** A spike recovery test was carried out to determine the level of silicon in a sample that could be analyzed without significant matrix suppression. For this test, external calibration curves in 4% HF and 6% HNO<sub>3</sub> solution were used to determine the concentration of each analyte in the various silicon samples. Example calibration curves for K and Ca are shown in Figures 2 and 3, respectively. As described earlier, the plasma temperature cannot

Table I. Operating Conditions for ELAN DRC ICP-MS

Parameter/System	Setting/Type
Nebulizer	PFA concentric type (ESI, Inc., Omaha, NE, USA)
Spray chamber	PFA double-Scott type (ESI, Inc., Omaha, NE, USA)
Torch	Sapphire injector
Sampling cone	Pt
Skimmer cone	Pt
RF power	1500 W
Plasma gas flow	16 L/min
Nebulizer gas flow	0.99 L/min
Sample uptake rate	30 µL/min
Reaction gas	Ammonia (Research grade, Matheson Gas Products Canada, ON, Canada)
Integration time	1 sec/mass
Replicates	3 or 7 (for DL calculation)

Table II. Analytes and Measurement Modes

Analytes	Measurement Mode
B, Na, Mg, Cu, Mo and Cd	Standard mode (without reaction gas)
Al, K, Ca, V, Cr, Mn, Fe, Ni, Co, and Zn	DRC mode (with reaction gas)

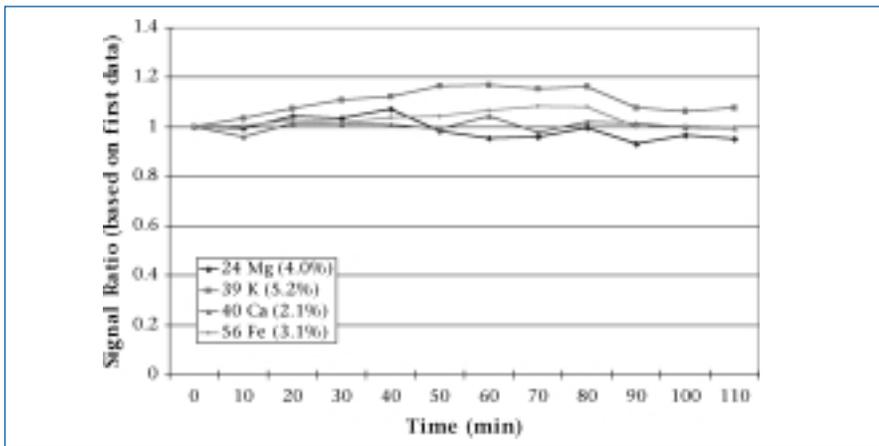


Figure 1. Two-hour stability test— continuous introduction of 0.5 ppb in 500 ppm Si.

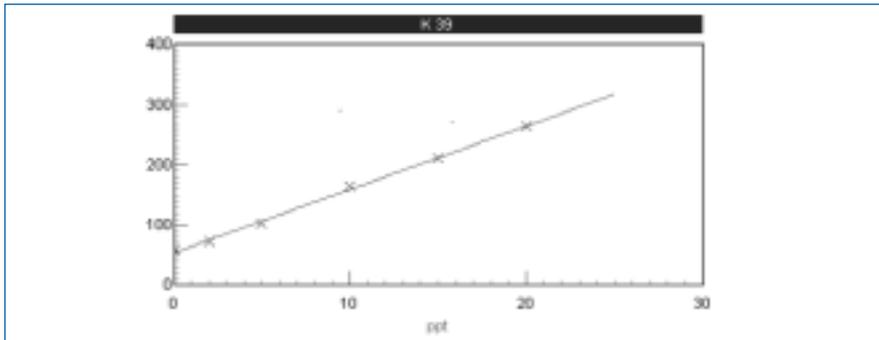


Figure 2. <sup>39</sup>K calibration curve.

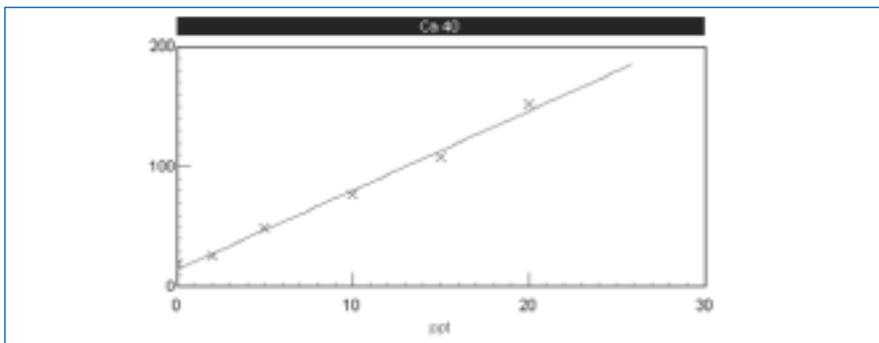


Figure 3. <sup>40</sup>Ca calibration curve.

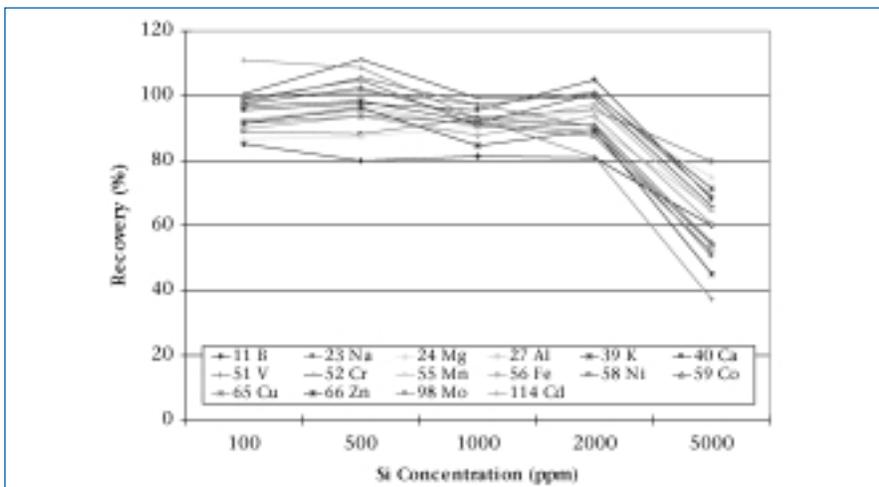


Figure 4. Summary of spike recovery tests (100 – 5000 ppm of Si).

be cooled enough using the cool plasma technique with a low-flow nebulizer which gives higher background. By contrast, the background level of the ELAN DRC system is not affected by the plasma temperature and as a result, the K and Ca background equivalent concentration (BEC) levels were only a few parts-per-trillion (ppt) with a sample uptake rate at 30  $\mu$ L/min.

An additional benefit of using hot plasma conditions for this particular sample matrix is the accelerated decomposition of polyatomic ions such as  $\text{CaF}_2$ , which are formed in the HF matrix. This species cannot be decomposed under cool plasma conditions and typically causes low sensitivity for Ca. However, using hot plasma conditions in the ELAN DRC, this species is decomposed and the Ca sensitivity is maintained.

The recovery results for the samples containing different concentrations of Si are summarized in Figure 4. This test shows that samples containing up to 2000 ppm Si can be analyzed against a simple external calibration curve that does not contain any Si. Also evident from this test is that a signal suppression of less than 20% occurs, which is excellent for this matrix type. The spike recovery results for the 2000 ppm Si sample using the external calibration curve are shown in Table III. These results indicate that most of the elements show greater than 90% spike recovery, which is excellent for this matrix, particularly since the calibration curve was prepared in an acid-only matrix.

The detection limits obtained in this experiment are also shown in Table III. They were calculated using three times the standard deviation of 4% HF/6%  $\text{HNO}_3$  blank solution. Since matrix-matched calibration curves are not required to analyze Si matrix samples, the detection limits achieved on the ELAN DRC are independent from the sample matrix and can be determined from the simple acid blank.

Table III. Spike Recovery Results for 2000 ppm of Si

Element	m/z	Unspiked Sample Measured Concentration (ppb)	Spike Amount (ppb)	Spiked Sample Measured Concentration (ppb)	Spike Recovery (%)	DL (ppt)
B	11	1.311	4.85	5.232	80.8	6.9
Na	23	1.055	4.85	5.696	95.7	1.9
Mg	24	0.045	4.85	4.675	95.5	1.1
Al	27	0.846	4.85	5.261	91.0	3.4
K	39	0.264	4.85	5.138	100.5	1.9
Ca	40	0.214	4.85	5.300	104.9	1.11
V	51	0.001	4.85	4.896	100.9	0.84
Cr	52	0.052	4.85	4.869	99.3	2.7
Mn	55	0.001	4.85	4.723	97.4	0.67
Fe	56	0.018	4.85	4.560	93.7	3.6
Ni	58	0.017	4.85	4.265	87.6	3.0
Co	59	0.003	4.85	4.414	90.9	0.72
Cu	65	0.034	4.85	4.351	89.0	5.1
Zn	66	0.048	4.85	4.380	89.3	7.7
Mo	98	0.005	4.85	4.385	90.3	2.0
Cd	114	0.001	4.85	3.938	81.2	0.98

## Conclusions

The data presented in this application note show that the ELAN DRC can effectively eliminate the  $^{40}\text{Ar}$  interference on  $^{40}\text{Ca}$ , the  $^{38}\text{Ar}^1\text{H}$  interference on  $^{39}\text{K}$ , and the  $^{40}\text{Ar}^{16}\text{O}$  interference on  $^{56}\text{Fe}$ , as well as other common troublesome interferences in ICP-MS using ammonia as the reaction gas. By adjusting the dynamic bandpass tuning parameters to eliminate unwanted reaction by-products, and combining DRC mode and standard mode elements in the same analytical method, 16 elements can be determined in the same sample analysis, increasing laboratory productivity. In addition, spike recovery tests demonstrate the ability of the ELAN DRC to perform these analyses utilizing robust hot plasma

conditions, significantly reducing matrix suppression effects. This means that the ELAN DRC can perform silicon analysis with minimal matrix suppression using a simple external calibration curve, unlike the previously used cool plasma method, where the sensitivity changes drastically as a function of Si concentration and matrix-matched standards or the method of standard additions is required. This attribute gives the ELAN DRC a tremendous advantage in performing ultratrace level determinations over cool plasma analysis. Even though the method of standard additions is used in cool plasma analysis, impurities in the acid blank used for sample preparation cannot be subtracted from the sample

because the sensitivities in the acid blank and in the silicon-containing sample matrix are quite different. This leads to higher background equivalent concentration (BEC) levels and inadequate detection limits using cool plasma analysis for silicon-containing matrices. Because the ELAN DRC uses robust hot plasma conditions all the time, matrix suppression is kept to a minimum, eliminating the need for matrix-matched standards. As a result, acid-only calibration curves can be used for high Si matrix samples containing up to 2000 ppm Si instead of the time-consuming method of standard additions.

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