

ICP - Mass Spectrometry

Author

Kenneth Ong

PerkinElmer, Inc.
Singapore

Determination of Impurities in Silica Wafers with the NexION 300S/350S 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, such as hydrofluoric acid (HF). Vapor phase decomposition is the most common method used for the surface analysis of silicon wafers and involves collecting impurities on the wafer surface using a very small amount of acid (typically HF) deposited on the surface as a droplet. This results in a typical sample volume of around 200 μL . For bulk silicon analysis, sample volume is not an issue; however, small sample volumes are desirable in order to minimize time-consuming sample preparation. As such, both types of silicon analyses require the ability to handle small sample volumes and high silicon matrices, as well as an HF-resistant sample introduction system. Since a typical analysis may take 2-3 minutes per sample, low-flow nebulizers with sample uptake rates from 20-100 $\mu\text{L}/\text{min}$ are routinely used.

Table 1. Instrumental parameters and sample introduction components for the NexION 300S ICP-MS.

| | | | |
|-----------------|------------------------|-------------------|------------------|
| Spray Chamber: | PFA Scott | Nebulizer: | 20 µL/min PFA-ST |
| Torch: | High Efficiency Quartz | Plasma Gas: | 18 L/min |
| Torch Injector: | PFA-Platinum | Auxiliary Gas: | 1.1 L/min |
| Sampler Cone: | Platinum | RF Power: | 1600 W |
| Skimmer Cone: | Platinum | Integration Time: | 1 sec/mass |

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 ArO^+ , ArH^+ , and Ar^+ . By providing a low flow of the proper reaction gas into the Universal Cell and using the unique Dynamic Bandpass Tuning (DBT) feature, both part of PerkinElmer's NexION® 300 ICP-MS, interferences can be chemically removed from the ion beam before they enter the analyzer quadrupole of the mass spectrometer. Another advantage of the NexION 300 ICP-MS is that it always operates under robust, hot plasma conditions, effectively decomposing the sample matrix. The NexION 300 ICP-MS also has the ability to combine elements run in Reaction mode (with reaction gas) with elements run in Standard mode (without a 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 (Reaction and Standard) are combined by the instrument's software and printed out in a single report.

This application note demonstrates the ability of the NexION 300S ICP-MS to analyze impurities in low-volume bulk silicon samples using a low-flow nebulizer.

Experimental Conditions

Sample Preparation: A bulk silicon sample was digested with a small amount of concentrated high-purity HF and HNO_3 acids. Typically, 0.1 g of crushed silica wafer is weighed into a clean, dry PTFE bottle, followed by the addition of 1 mL of HF and 0.5 mL of HNO_3 . The addition of HNO_3 should be done with small, successive aliquots because of the high reactivity involved. No heating is necessary; the addition of HF and HNO_3 will dissolve the silicon.

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 2% HF and 1.5% HNO_3 . Two samples were prepared for each Si concentration, and one of each pair was spiked with a standard solution (PerkinElmer Pure, PerkinElmer, Shelton, CT, USA) in order to perform spike recovery tests. Calibration solutions in 2% HF and 1.5% HNO_3 (Tama Chemicals, Tokyo, Japan) were prepared from multi-element solutions (PerkinElmer Pure, PerkinElmer, Shelton, CT, USA).

Instrumental Conditions: The instrument used was the PerkinElmer® NexION 300S ICP-MS. The instrument operating conditions and sample introduction system used for this work are shown in Table 1.

The elements determined and instrument modes used are shown in Table 2.

Table 2. Analytes and the measurement modes.

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

Results

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 NexION 300S ICP-MS to use hot plasma conditions for all analyses greatly reduces this signal drift. In order to show the benefit of using the more robust hot plasma conditions, a 2000-ppm silicon sample spiked with a 100-ppt multi-element standard solution was continuously introduced into the NexION 300S without washing for two hours, while taking readings every 5 minutes. As shown in Figures 1 and 2, the signal for elements in Standard and Reaction modes (in a single method) were very stable even during constant nebulization of the sample solution.

For quantitative measurements, additions calibrations with 2000 ppm of silica in 2% HF and 1.5% HNO₃ solution were used to determine the concentration of each analyte in the various silicon samples. Calibration curves for Ca, Fe and Co are shown in Figures 3–5, respectively.

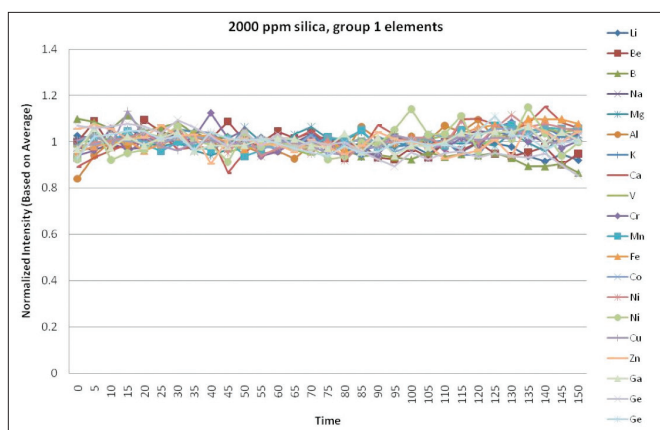


Figure 1. Continuous analysis of 100 ppt multielements spike in 2000-ppm silica solution, first group.

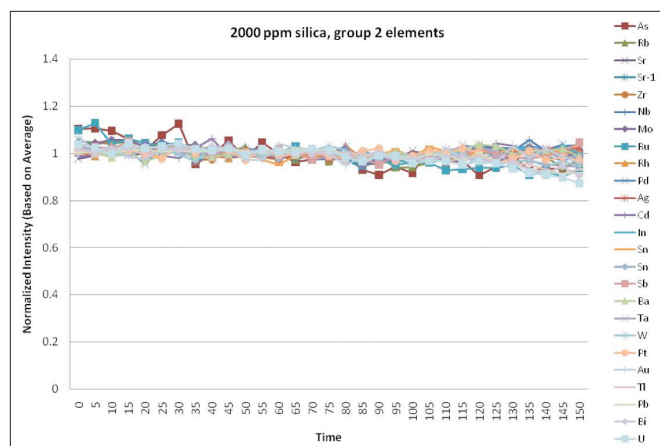


Figure 2. Continuous analysis of 100 ppt multielements spike in 2000-ppm silica solution, second group.

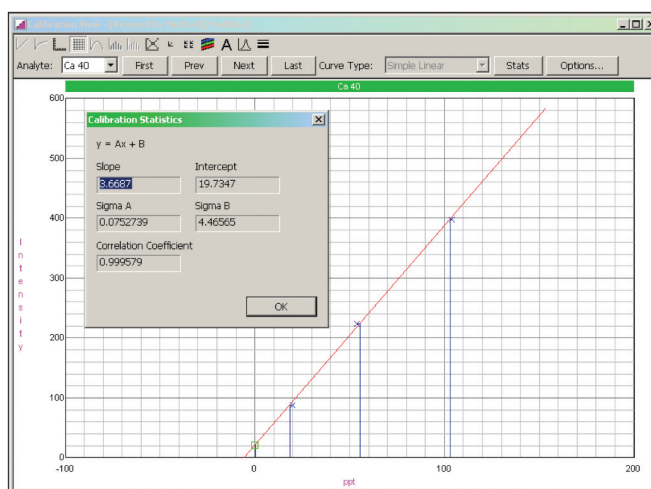


Figure 3. Ca calibration, with NH₃ cell gas flow of 1 mL/min.

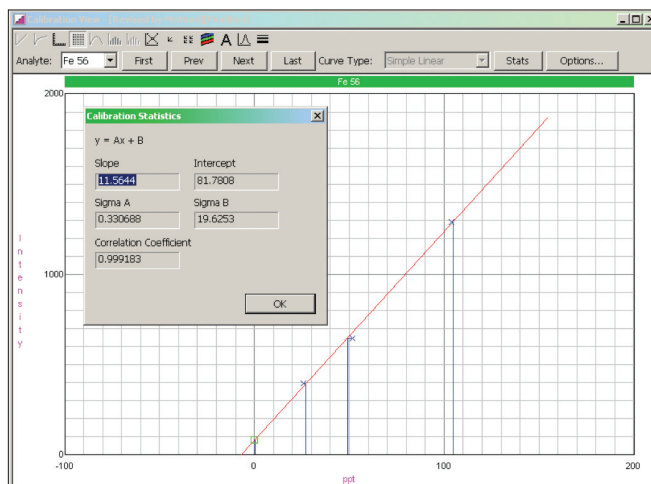


Figure 4. Fe calibration, with NH₃ cell gas flow of 0.6 mL/min.

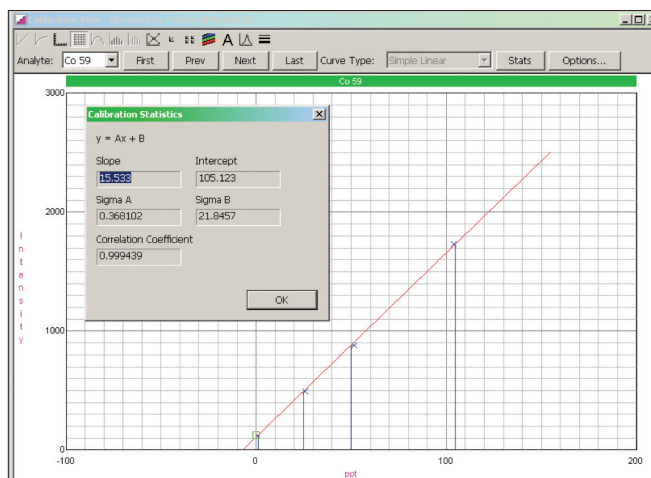


Figure 5. Co calibration, with NH₃ cell gas flow of 0.3 mL/min.

It can be deduced from the calibration plots that the background level of the NexION 300S system is not affected by the plasma temperature, and as a result, the Ca, Fe and Co background equivalent concentration (BEC) levels were only a few parts per trillion (ppt), with a sample uptake rate at 20 $\mu\text{L}/\text{min}$. The benefit of using hot plasma conditions for this particular sample matrix is the accelerated decomposition of polyatomic ions such as CaF_2 , which are formed in the HF matrix. This species cannot be decomposed under cool plasma conditions, typically causing low sensitivity for Ca. However, using hot plasma conditions in the NexION 300S, this species is effectively decomposed, and the Ca sensitivity is maintained. Furthermore, the use of Reaction mode in the Universal Cell eliminated the ArF^+ polyatomic interference on Co, allowing low-levels to be measured.

A spike recovery test was carried out to determine the level of silicon in a sample that could be analyzed without significant matrix suppression. The recovery results for the samples containing different concentrations of Si with a 100 ppt multielement spike are summarized in Figure 6. This test shows that samples containing up to 5000 ppm Si can be analyzed against an additions calibration curve containing 2000 ppm of Si. Also evident from this test is that a signal suppression of less than 20% occurs, which is excellent for this matrix type.

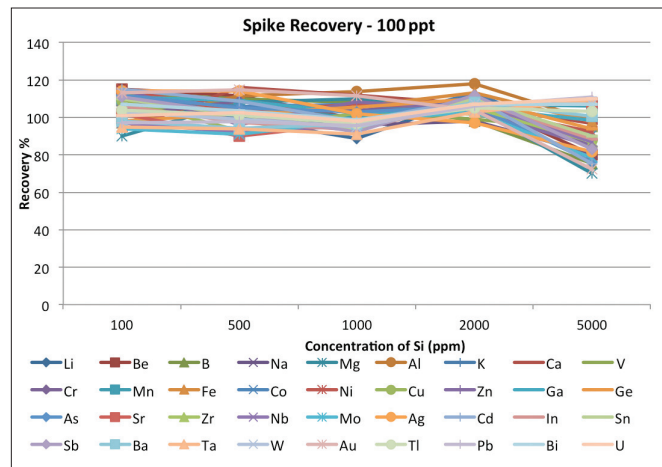


Figure 6. Spike recovery tests of 100 ppt multielement standard in silica matrix ranging from 100 ppm to 5000 ppm.

A separate spike recovery test of a 50-ppt multielement spike into 2000-ppm silicon was carried out. The results are shown in Table 3 and indicate that all of the elements show greater than 90% spike recovery, which is excellent for this matrix. Table 3 also shows detection limits, which were calculated using three times the standard deviation of the 2000-ppm Si in 2% HF/1.5% HNO_3 blank solution. Since matrix-matched calibration curves are not required to analyze Si matrix samples, the detection limits achieved on the NexION 300S ICP-MS are independent of the concentration of Si in the solution.

Table 3. Detection limits (DLs) and 50 ng/L spike recoveries for all analytes in 2000-ppm Si solution (units in ng/L).

| Analyte | Mass | Cell Gas Flow* (mL/min) | RPq | DL (ppt) | 50 ppt Recovery |
|---------|------|----------------------------|------|-------------|--------------------|
| Li | 7 | 0 | 0.25 | 2.6 | 110% |
| Be | 9 | 0 | 0.25 | 5 | 101% |
| B | 11 | 0 | 0.25 | 5.8 | 97% |
| Na | 23 | 0 | 0.25 | 2 | 106% |
| Mg | 24 | 0 | 0.25 | 1.9 | 111% |
| Al | 27 | 0.6 | 0.5 | 4 | 107% |
| K | 39 | 0.6 | 0.5 | 2 | 107% |
| Ca | 40 | 1 | 0.5 | 1.7 | 109% |
| V | 51 | 0.3 | 0.5 | 0.9 | 93% |
| Cr | 52 | 0.3 | 0.5 | 3 | 97% |
| Mn | 55 | 0.6 | 0.7 | 0.7 | 105% |
| Fe | 56 | 0.6 | 0.5 | 2.8 | 103% |
| Co | 59 | 0.3 | 0.5 | 0.8 | 99% |
| Ni | 60 | 0.3 | 0.7 | 3 | 96% |
| Cu | 63 | 0.3 | 0.5 | 3.5 | 98% |
| Zn | 64 | 0.3 | 0.65 | 4.2 | 105% |
| Ga | 71 | 0.6 | 0.5 | 3 | 97% |
| Ge | 74 | 0.3 | 0.65 | 4 | 110% |
| As | 75 | 0 | 0.25 | 10 | 96% |
| Sr | 88 | 0.6 | 0.5 | 1.5 | 103% |
| Zr | 90 | 0 | 0.25 | 2.8 | 101% |
| Nb | 93 | 0 | 0.25 | 1.8 | 103% |
| Mo | 98 | 0 | 0.25 | 2 | 102% |
| Ag | 107 | 0 | 0.25 | 1 | 115% |
| Cd | 114 | 0 | 0.25 | 1 | 110% |
| In | 115 | 0 | 0.25 | 1.6 | 109% |
| Sn | 120 | 0 | 0.25 | 2 | 110% |
| Sb | 121 | 0 | 0.25 | 2 | 110% |
| Ba | 138 | 0 | 0.25 | 1.6 | 104% |
| Ta | 181 | 0 | 0.25 | 2 | 99% |
| W | 184 | 0 | 0.25 | 2 | 99% |
| Au | 197 | 0 | 0.25 | 3 | 98% |
| Tl | 205 | 0 | 0.25 | 1.8 | 100% |
| Pb | 208 | 0 | 0.25 | 1.7 | 103% |
| Bi | 209 | 0 | 0.25 | 2 | 102% |
| U | 238 | 0 | 0.25 | 2.8 | 100% |

*Cell gas used is NH_3 .

Conclusion

The data presented in this application note show that the NexION 300S ICP-MS can effectively eliminate the $^{40}\text{Ar}^+$ interference on $^{40}\text{Ca}^+$, the $^{40}\text{Ar}^{19}\text{F}^+$ interference on $^{59}\text{Co}^+$, 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 byproducts and combining Reaction mode and Standard mode elements in the same analytical method, multiple elements can be determined in the same sample analysis, increasing laboratory productivity. In addition, spike recovery tests demonstrate the ability of the NexION 300S ICP-MS to perform these analyses utilizing robust hot plasma conditions, significantly reducing matrix suppression effects with silica matrix up to 2000 ppm. This means that the NexION 300S ICP-MS can perform silicon analysis with minimal matrix suppression using a simple external calibration curve.