

Determination of ultratrace elements on silicon wafer surfaces using the Thermo Scientific iCAP TQs ICP-MS

Authors

Tomoko Vincent,
Product Specialist,
Thermo Fisher Scientific

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Goal

To determine ultratrace metal concentrations in semiconductor silicon wafer vapor phase decomposition (VPD) samples use cold plasma and triple quadrupole technologies to reduce background equivalent concentrations (BEC) and detection limits (LOD). Demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS perform reproducible ultratrace $\text{ng}\cdot\text{L}^{-1}$ (ppt) measurements with reliable switching between multiple analysis modes (hot/cold plasma, single/triple quadrupole) within a single measurement.

Introduction

With the continual decrease in device geometries, the maximum allowable trace metallic impurity levels in process materials, as defined by Semiconductor Equipment and Materials International (SEMI), are moving to lower levels.

The most widely used semiconductor material is silicon wafer, which is required to be greater than 99.9999999% pure silicon (9N purity). Monitoring trace element contamination of the wafer surface is a routine requirement in the semiconductor industry. Common methods for this analysis are total reflection x-ray fluorescence (TR-XRF) and vapor phase decomposition inductively coupled plasma mass spectrometry (VPD-ICP-MS).

TR-XRF is well accepted in the semiconductor industry because it is a non-destructive technique. However, this technique can only monitor the surface of silicon wafer materials which are coated in oxide and nitride films and detection limits of 10^{10} to 10^{12} atoms cm^{-2} do not meet requirements of the latest wafer production technologies.

In contrast, the VPD technique etches the film layer on the wafer surface prior to using a drop of concentrated acid scanned across the etched wafer surface to allow contamination in the pure Si material to be evaluated. This approach improves detection limits by more than two orders of magnitude compared to TR-XRF.

VPD with ICP-MS detection provides the required detection capability, method robustness, speed and reliability for routine and reproducible analysis, so the combination of these technologies is widely applied in silicon wafer manufacturing facilities.

Typical VPD samples contain high acid and silicon concentrations and the target analyte concentrations are very low. This makes the ICP-MS challenging as the sample matrix generates significant polyatomic interferences on the target elements (see Table 1). To obtain accurate results, elimination of these interferences using advanced technology such as triple quadrupole ICP-MS or high resolution ICP-MS is required.

This application note demonstrates the performance achieved for the analysis of VPD samples using the iCAP TQs triple quadrupole ICP-MS.

Table 1. Typical target analytes with commonly observed interferences.

Analyte	Matrix-Based Interferences
^{48}Ti	$^{28}\text{Si}^{19}\text{F}^{\dagger}\text{H}$, $^{29}\text{Si}^{19}\text{F}$
^{56}Fe	$^{28}\text{Si}^{28}\text{Si}$
^{60}Ni	$^{28}\text{Si}^{16}\text{O}^{16}\text{O}$
^{63}Cu	$^{28}\text{Si}^{16}\text{O}^{19}\text{F}$
^{66}Zn	$^{28}\text{Si}^{19}\text{F}^{19}\text{F}$
^{74}Ge	$^{29}\text{Si}^{29}\text{Si}^{16}\text{O}$



Instrumentation

An iCAP TQs ICP-MS was used for all measurements. The sample introduction system used comprised of a double pass PFA spraychamber, a PFA $100 \mu\text{L}\cdot\text{min}^{-1}$ self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) nebulizer and a quartz torch and 2.0 mm i.d. removable sapphire injector. Platinum tipped sample and skimmer cones with cold plasma extraction lens were used.

The instrument was operated in SQ-KED, SQ-CP-NH₃ (cold plasma with NH₃ reaction gas) and TQ using pure O₂ (TQ-O₂) modes.

Table 2 summarizes the instrument configuration and operating parameters. Measurement modes were optimized using the default autotune procedures in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Table 2. Instrument configuration and operating parameters.

Parameter	Value		
Nebulizer	PFA concentric nebulizer	$100 \mu\text{L}\cdot\text{min}^{-1}$	(self-aspirating)
Spraychamber	High sensitivity PFA double pass spraychamber		
Injector	2.0 mm i.d., sapphire		
Interface	Pt sample and Pt skimmer high sensitivity type		
Extraction lens	Cold plasma lens		
Measurement mode	Single quad mode		Triple quad mode
	SQ-CP-NH ₃	SQ-KED	TQ-O ₂
Forward power	520 W	1550 W	1550 W
Nebulizer gas	$0.965 \text{ mL}\cdot\text{min}^{-1}$	$0.999 \text{ mL}\cdot\text{min}^{-1}$	$0.999 \text{ mL}\cdot\text{min}^{-1}$
CRC gas	Pure NH ₃ $0.28 \text{ mL}\cdot\text{min}^{-1}$	Pure He $4.2 \text{ mL}\cdot\text{min}^{-1}$	Pure O ₂ $0.3 \text{ mL}\cdot\text{min}^{-1}$
Dwell time	100 to 300 ms per analyte, 5 sweeps		

Sample preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water ($18.2\text{ M}\Omega\text{ cm}$) and left to dry in a laminar flow clean hood before use. A silicon wafer was used for this study to prepare the simulated VPD sample. To digest the sample, 10 g hydrofluoric acid (50% Optima grade, Fisher Chemical) and 10 g nitric acid (68% Optima grade, Fisher Chemical) were first added gently to approximately 1.7 g of silicon wafer in a PFA sample preparation bottle. Ultrapure water (65 g) was subsequently added. The final analysis sample solution was then prepared by dilution with ultrapure water to provide a $200\text{ mg}\cdot\text{L}^{-1}$ Si matrix comparable to that produced by VPD.

Standards at concentrations of 25, 50 and 100 $\text{ng}\cdot\text{L}^{-1}$ were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (SPEXCertiPrep™) directly to aliquots of the $200\text{ mg}\cdot\text{L}^{-1}$ Si matrix sample. Semiconductor grade 0.5% (m/m) hydrofluoric acid and 0.1% (m/m) nitric acid were used for the rinse solutions. Recovery tests were performed using $50\text{ ng}\cdot\text{L}^{-1}$ spikes.

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for multi-element analysis in semiconductor (or any other high purity chemical) applications. By providing the analyst with unlimited flexibility of ICP-MS technologies (cold plasma, kinetic energy discrimination or triple quadrupole), the ultimate performance can be achieved, specifically tailored for each application.



Figure 1. Thermo Scientific iCAP TQs ICP-MS.

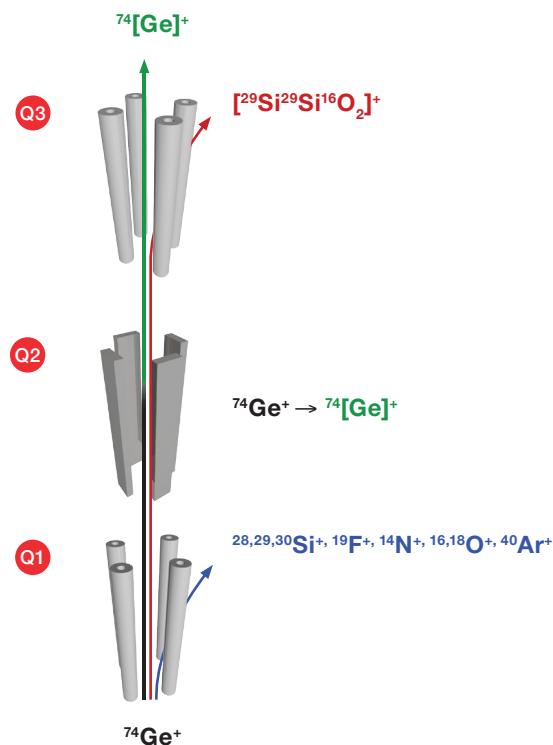
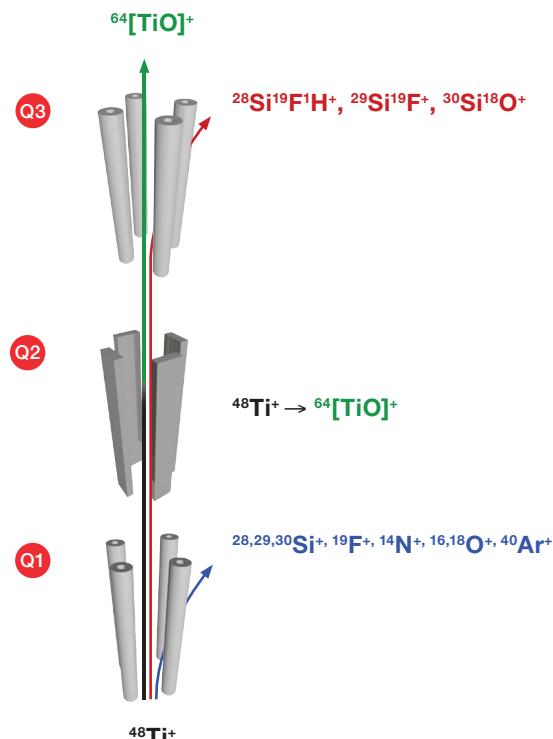


Figure 2. Schematic showing TQ O₂ **mass shift** mode for titanium and TQ O₂ **on mass** mode for germanium.

For example, using the TQ-O₂ mass shift mode (shown in upper diagram in Figure 2 with Ti as an example), Si, N, O and F based polyatomic interferences are efficiently removed providing accurate analysis of Ti. In TQ-O₂ mass shift mode, the first quadrupole (Q1) uses intelligent mass selection (iMS) to reject unwanted ions. The second quadrupole (Q2) is used to selectively shift the Ti target analytes to the TiO⁺ product ions using O₂ as the reaction gas, while the potential interferences do not react with O₂. The third quadrupole (Q3) then isolates the TiO⁺ product ions and removes any remaining interferences through a second stage of mass filtration allowing completely interference free analysis of the analyte to be achieved.

In the second example, germanium in a silicon matrix is analyzed in the TQ-O₂ on mass mode (shown in the lower diagram in Figure 2). Here the SiO interference is preferentially oxidized in the Q2 CRC to higher oxides, whilst the germanium does not react and is therefore isolated by Q3 at measured the original Ge isotope mass.

Table 3. LOD, measurement results, recovery and reproducibility (n=5) for the analysis of a silicon matrix sample. Please note that LOD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible.

	Analysis mode	LOD (ng·L⁻¹)	Measurement results (ng·L⁻¹)	50 ng·L⁻¹ recovery (%)	Reproducibility (n=5) (%)
⁷ Li	SQ-CP-NH ₃	0.1	0.02	98%	95.2±3.7
²³ Na	SQ-CP-NH ₃	0.6	2.3	100%	100.2±1.5
²⁴ Mg	SQ-CP-NH ₃	0.3	0.4	99%	98.3±2.2
²⁷ Al	SQ-CP-NH ₃	1.3	6.0	104%	105.2±3.1
³⁹ K	SQ-CP-NH ₃	0.6	1.0	98%	101.0±1.5
⁴⁰ Ca	SQ-CP-NH ₃	1.0	4.1	103%	101.4±4.1
⁴⁸ Ti at 64 m/z	TQ-O ₂	1.2	2.8	99%	105.7±1.5
⁵¹ V at 67 m/z	TQ-O ₂	0.2	0.8	98%	103.1±1.6
⁵⁵ Mn	SQ-CP-NH ₃	2.3	3.5	97%	103.8±1.9
⁵⁶ Fe	SQ-CP-NH ₃	1.6	3.4	98%	102.2±3.3
⁵⁹ Co	SQ-CP-NH ₃	0.9	2.2	97%	99.0±2.3
⁶³ Cu	SQ-CP-NH ₃	0.9	1.7	98%	99.5±1.2
⁶⁶ Zn	SQ-KED	1.9	7.7	90%	111.1±3.4
⁷¹ Ga	SQ-KED	1.2	2.3	91%	106.9±4.4
⁷⁴ Ge at 74 m/z	TQ-O ₂	1.0	2.7	100%	104.1±1.2
⁷⁵ As at 91 m/z	TQ-O ₂	0.4	0.7	101%	106.0±2.5
⁸⁸ Sr	SQ-KED	0.2	0.1	98%	105.2±2.8
⁹⁰ Zr	SQ-KED	0.1	0.1	96%	105.7±2.6
⁹⁸ Mo	SQ-KED	0.5	1.1	93%	107.0±3.8
¹⁰⁷ Ag	SQ-KED	0.3	1.0	95%	107.0±4.0
¹¹¹ Cd	SQ-KED	0.4	0.6	95%	111.1±4.5
¹¹⁸ Sn	SQ-KED	0.3	0.6	93%	107.9±4.0
¹²¹ Sb	SQ-KED	0.1	0.1	93%	105.3±2.0
¹³⁸ Ba	SQ-KED	0.1	0.1	93%	105.7±4.5
¹⁸⁴ W	SQ-KED	0.1	0.2	93%	103.6±3.8
²⁰⁸ Pb	SQ-KED	0.3	1.2	91%	107.2±4.1

As can be seen in the measurement results (Table 3), LOD values (calculated from three times the standard deviation of ten replicate measurements of the calibration blank), spike recovery and reproducibility of Si matrix samples (100 ng·L⁻¹ spiked, n=5) were determined for 26 elements in the VPD sample. Accurate spike recoveries from 90% to 104% were obtained for all 26 elements at 50 ng·L⁻¹.

Although the sample contains 200 mg·L⁻¹ silicon matrix, excellent reproducibility and reliability was achieved, with ±2.2% RSD for 5 replicates, demonstrating the robustness of the iCAP TQs ICP-MS in mixed hot and cold plasma analyses.

Calibration curves

Calibration curves for Li, K, Ca Ti, V and As in Si 200 mg·L⁻¹ are shown in Figure 3. The calibrations, performed with calibration standards in the ng·L⁻¹ range, showed excellent linearity and sensitivity. The low backgrounds achieved for the more challenging analytes such as ⁴⁸Ti was possible through improved interference removal with triple quadrupole modes and cold plasma operation.

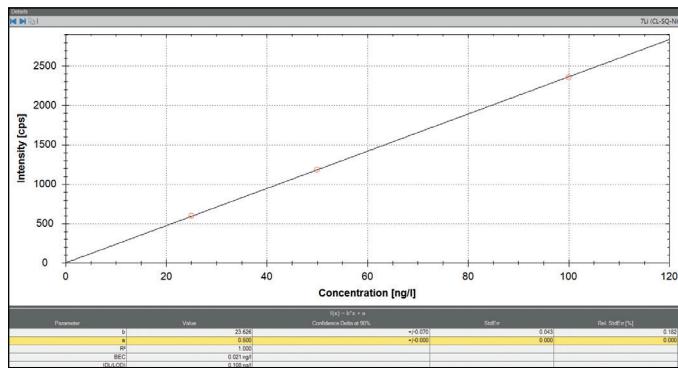


Figure 3a. Li in SQ-CP-NH₃ mode.

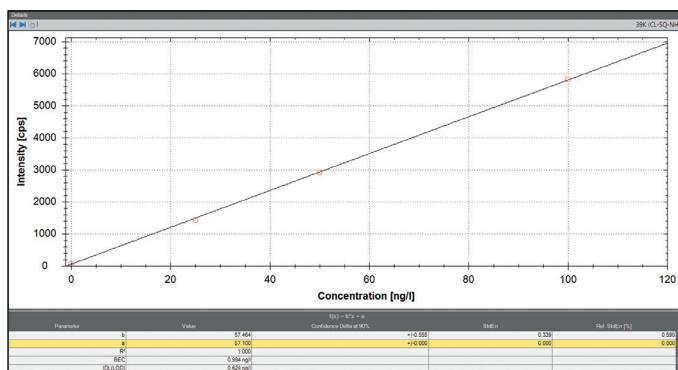


Figure 3b. K in SQ-CP-NH₃ mode.

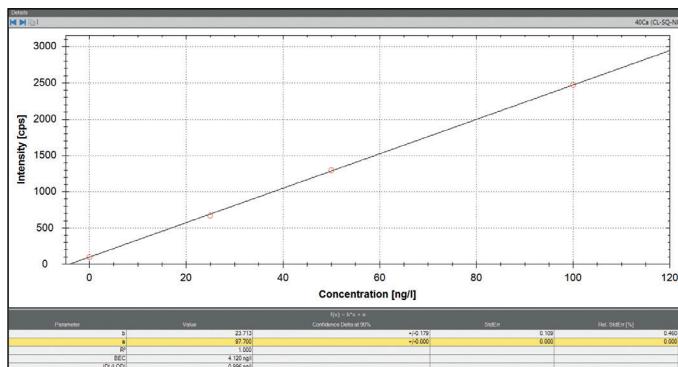


Figure 3c. Ca in SQ-CP-NH₃ mode.

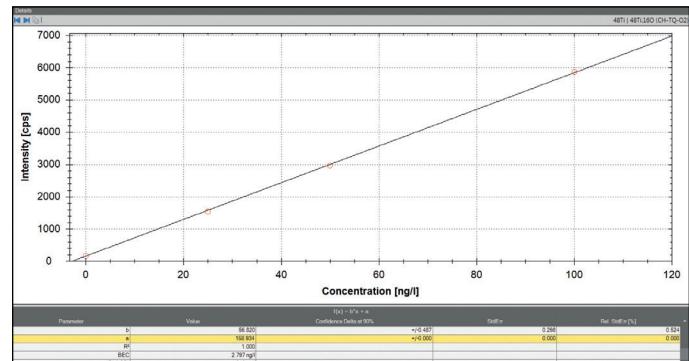


Figure 3d. Ti in TQ-O₂ mass shift mode.

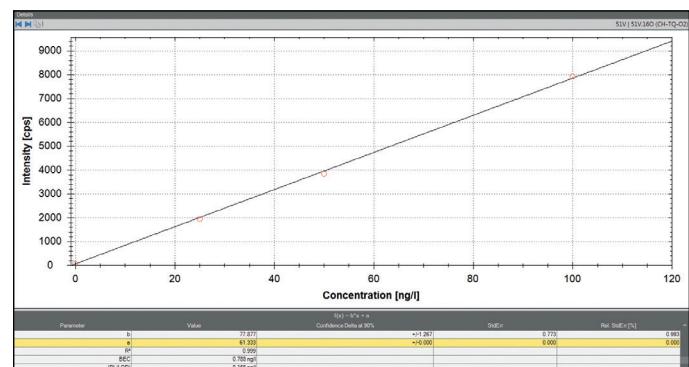


Figure 3e. V in TQ-O₂ mass shift mode.

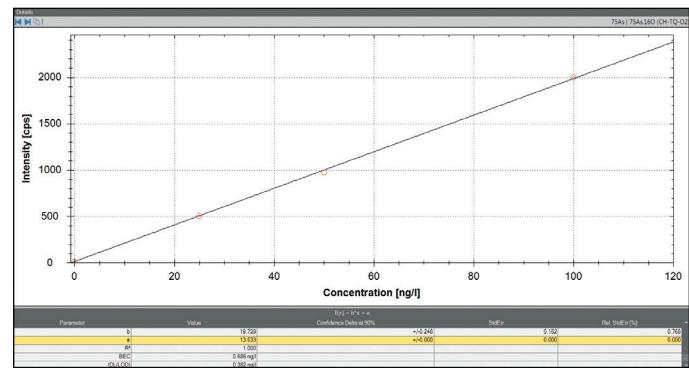


Figure 3f. As in TQ-O₂ mass shift mode.

Conclusions

The Thermo Scientific iCAP TQs ICP-MS has been shown to provide sensitive and accurate multi-element analysis of synthetic VPD samples at ultratrace ($\text{ng}\cdot\text{L}^{-1}$) concentration levels. The combination of single and triple quadrupole technologies, with and without cold plasma operation, delivers the flexibility required to deliver optimum analysis conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching of the iCAP TQs ICP-MS between multiple analysis modes enables smooth transitions between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.

Find out more at thermofisher.com/TQ-ICP-MS

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