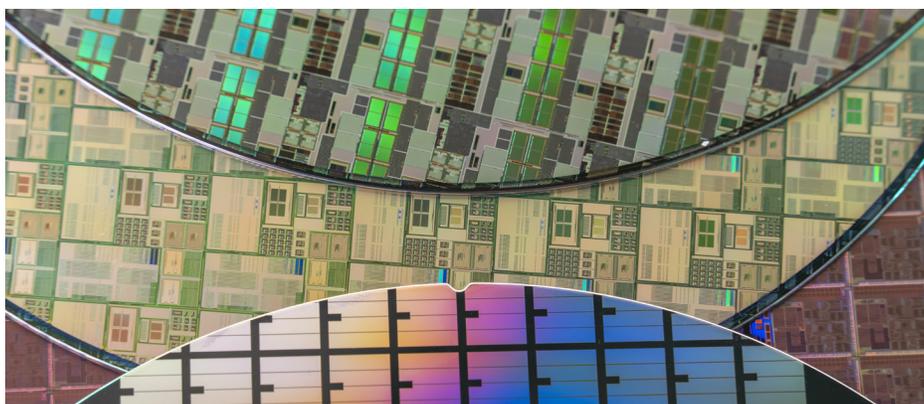


Analysis of 50 nm Silica Nanoparticles in Semiconductor Process Chemicals by spICP-MS/MS

Accurate detection of insoluble SiO_2 NPs in high purity acids and solvents by Agilent 8900 ICP-QQQ



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Introduction

The fabrication of smaller, denser, more power-efficient integrated circuits (ICs) with higher-performance characteristics requires a reliable supply of ultra-high purity materials and reagents (1). While dissolved elements are routinely monitored in process chemicals during IC manufacturing, contamination from even 50 to 60 nm particles can cause circuit defects and device or chip failures. To maximize yields, some semiconductor manufacturers and chemical suppliers are beginning to measure nanoparticles (NPs) as well as dissolved elements in reagents (2, 3). Contaminants, including NPs, can be introduced from raw materials and from processing equipment. Silicon dioxide (SiO_2) NPs are potentially problematic to IC performance as they are insoluble in strong acids such as hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) and organic solvents such as isopropyl alcohol (IPA). These chemicals are used as cleaning solutions during IC fabrication so are in direct contact with the chips. To minimize cross-contamination from reagents to ICs, the industry needs a method that can accurately measure SiO_2 NPs in semiconductor grade chemicals. It is also important that the method can be integrated into the routine quality control/quality assurance (QC/QA) program for the determination of elemental impurities in reagents.

A highly sensitive analytical technique such as ICP-MS is commonly used to determine metal contaminants in the high purity chemicals used in semiconductor manufacturing. ICP-MS can be used in single particle (sp) mode for the analysis of NPs. However, there are several challenges to overcome for the analysis of SiO₂ NPs using spICP-MS including:

- Removal of intense interferences such as N₂ and CO on the major isotope of Si (²⁸Si).
- Reduction of the Si background arising from the materials used within the ICP-MS instrument and utilities such as argon (Ar) gas or gas pipes.
- Achieving the sensitivity needed for the measurement of Si. Si has a relatively high ionization potential (IP) meaning that fewer ions form in the plasma compared with many other elements, lowering its sensitivity.

Since its launch in 2012, triple quadrupole ICP-MS (ICP-QQQ) has been accepted as the standard technique for monitoring elemental contamination in semiconductor chemicals. The Agilent 8900 ICP-QQQ provides a double mass selection capability, commonly termed MS/MS, via two quadrupole mass filters (Q1 and Q2) located either side of the Octopole Reaction System (ORS⁴) cell. MS/MS ensures excellent selectivity for Si through the elimination of the N₂ and CO interferences at mass 28 using hydrogen (H₂) gas in the ORS⁴ cell (4). To alleviate the Si background arising from the Ar gas supply, a special gas flow system for the 8900 Semiconductor configuration ICP-QQQ can be used. The inherently high sensitivity (low signal-to-noise) of the 8900 is key to the successful determination of SiO₂ NPs.

spICP-MS is a powerful NP characterization tool that is increasingly used in the semiconductor industry for the measurement of semiconductor grade chemicals (2–5). spICP-MS simultaneously determines the number, concentration, and size of particles, as well as the dissolved element concentration of samples. The Single Nanoparticle Application Module of the Agilent ICP-MS MassHunter software enables the 8900 ICP-QQQ to perform automated data analysis of NPs in spICP-MS mode.

In this work, SiO₂ NPs were measured in semiconductor grade HCl, H₂SO₄, and IPA using the 8900 ICP-QQQ operating in spICP-MS mode.

Experimental

Sample preparation

All samples were supplied as ultrapure grade. The samples were prepared in precleaned PFA containers. 98% H₂SO₄ was diluted 100 times (100x) or 200x using ultrapure water (UPW), depending on the test and 36% HCl was diluted 5x in UPW. IPA was not diluted before analysis.

Standards containing 50, 60, and 100 nm SiO₂ NPs were bought from nanoComposix Inc (San Diego, CA USA). The 100 nm SiO₂ NPs were used as a reference material for the calculation of the nebulization efficiency. To evaluate the accuracy of the spICP-MS method for the determination of particle size, the 50, 60, and 100 nm SiO₂ NP standards were added to the diluted acids and undiluted IPA.

Instrumentation

An 8900 ICP-QQQ (#200, Semiconductor configuration) and Agilent SPS 4 autosampler were used for all measurements. The sample introduction system comprised a standard quartz torch (2.5 mm i.d. injector for acids, 1.5 mm i.d. injector for IPA), quartz spray chamber, and platinum-tipped interface cones. The samples were self-aspirated using an Agilent PFA nebulizer and SPS 4 autosampler as described in a previous study (5).

The 8900 ICP-QQQ was operated in MS/MS mode for all Si measurements and H₂ cell gas was used to eliminate any polyatomic interferences on ²⁸Si from ¹⁴N₂ and ¹²C¹⁶O. ¹⁴N₂ and ¹²C¹⁶O ions react readily with H₂ in the cell, while Si ions do not react or react at a much slower rate. Both quadrupoles (Q1 and Q2) were set to *m/z* 28, enabling ²⁸Si⁺ to be measured free from the interferences at its original mass (6). Analysis was performed in fast Time Resolved Analysis (fast TRA) mode using a dwell time of 0.1 ms. Data analysis was performed using the optional Single Nanoparticle Application module of ICP-MS MassHunter software. The general settings of the 8900 ICP-QQQ are detailed in Table 1.

Table 1. Agilent 8900 ICP-QQQ general operating parameters.

Parameter	Value	
	HCl, H ₂ SO ₄	IPA
RF Power (W)	1200	
Sampling Depth (mm)	9	16
Nebulizer Gas Flow Rate (L/min)	0.8	0.75
Makeup Gas Flow Rate (L/min)	0.41	0.48
Option Gas (50% O ₂ /50% Ar)	NA	12.0% (0.12 L/min)
Sample Uptake Rate (mL/min)	0.22	0.27
Dwell Time (ms)	0.1	
Axial Acceleration (V)	2	
Energy discrimination (V)	-8.0	
Acquired Mass Number	28 for Q1 and Q2	
Cell Gas	Hydrogen	
Cell Gas Flow Rate (mL/min)	5.0	

Results and discussion

SiO₂ NP analysis in ultrapure water

To assess the effectiveness of the 8900 spICP-QQQ method for the determination of SiO₂ NPs, a mixture of approximately 10 ppt of 50 nm and 100 ppt of 100 nm SiO₂ NPs were added to UPW. Figure 1 shows the typical signals from the mixed-sized SiO₂ NPs in UPW. Smaller peaks (ranging from 1 × 10⁵ to ~2 × 10⁵ cps) from the 50 nm SiO₂ NPs can be observed among the larger peaks (0.8 × 10⁶ to ~1.4 × 10⁶ cps) from the 100 nm SiO₂ NPs. Figure 2 shows the signal and size distribution results from the 50 and 100 nm SiO₂ NPs. The size distribution plot shows good resolution between the 50 and 100 nm particles. The mean sizes of the SiO₂ NPs measured in UPW using the spICP-QQQ method were 50 and 99 nm, respectively. The results confirm the viability of the method for the analysis of SiO₂ NPs in more complex matrices.

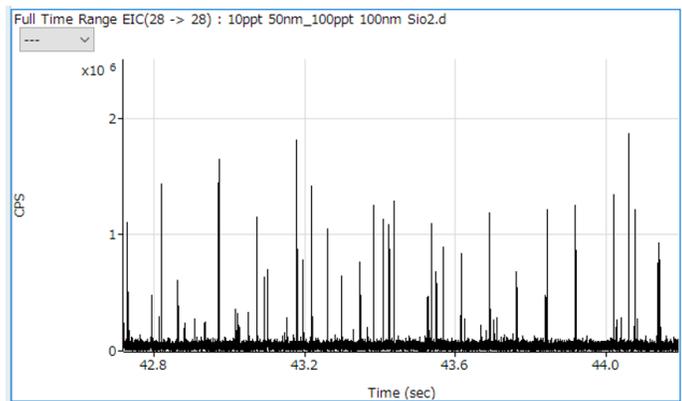


Figure 1. 50 and 100 nm SiO₂ signal NP events acquired in fast TRA mode using the Agilent 8900 ICP-QQQ.

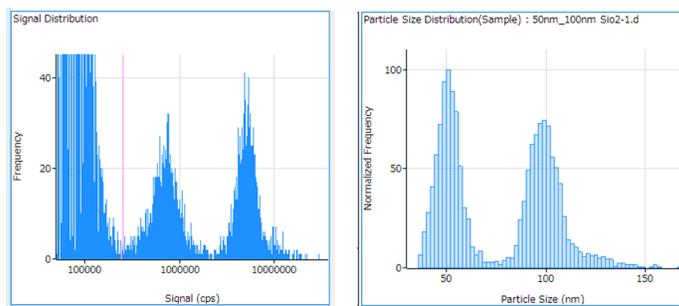


Figure 2. Signal distribution (left) and size distribution (right) of 50 and 100 nm SiO₂ NPs in UPW.

SiO₂ NP analysis in diluted HCl and H₂SO₄

To evaluate the performance of the 8900 spICP-QQQ method for the analysis of SiO₂ NPs in high purity acids, 50 nm SiO₂ NPs were added to 7.2% (5x diluted) HCl or 1% (100x diluted) H₂SO₄.

As shown in the signal distribution plot for the blank 7.2% HCl sample, no SiO₂ particles were detected (Figure 3 top left). When 20 ppt of 50 nm SiO₂ NPs were added to the 7.2% HCl solution, clear signal distribution and particle distribution plots were obtained, as shown in Figure 3, bottom left and right, respectively. The red line in Figure 3 represents the threshold that separates single NP signals from the background or from ionic signals. The threshold is set automatically by the ICP-MS MassHunter software. The quantitative result for the SiO₂ NPs measured in the 20 ppt spiked 7.2% HCl sample was automatically calculated by the Single Nanoparticle Application Module software as 22 ppt. The excellent recovery confirms that 50 nm SiO₂ particles can be measured with good accuracy of NP size and concentration in HCl.

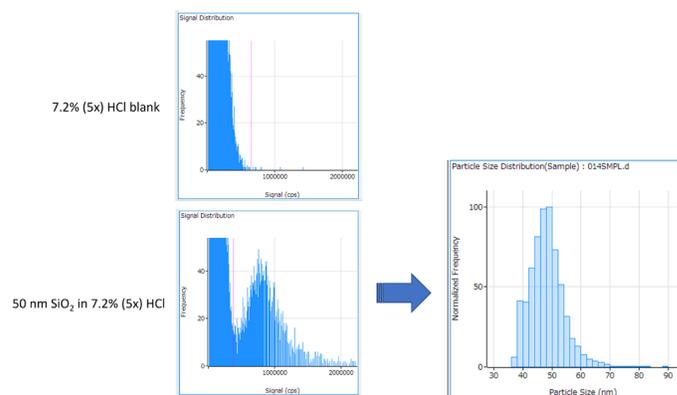


Figure 3. Distribution profiles of 50 nm SiO₂ in 7.2% HCl. Top left: signal distribution of HCl blank. Bottom left: signal distribution of 50 nm SiO₂ NPs added to HCl. Bottom right: particle size distribution of 50 nm SiO₂ NPs in HCl.

Figure 4 shows the signal distribution (left) and particle distribution (right) for 50 nm SiO₂ NPs added to 1% H₂SO₄. Despite the matrix, the signals from the 50 nm SiO₂ were clearly separated from the background signals.

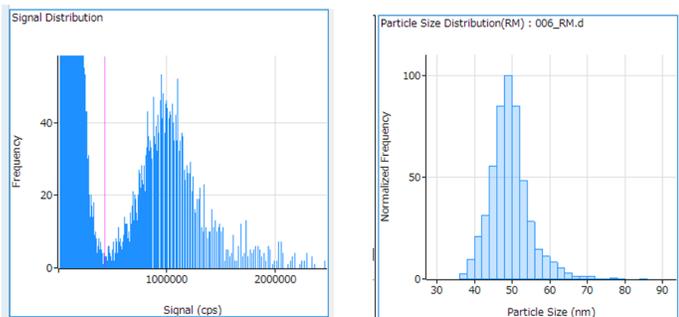


Figure 4. Signal distribution (left) and particle distribution (right) for 50 nm SiO₂ NPs in 1% H₂SO₄.

Long-term SiO₂ NP measurement in H₂SO₄

To test the stability of measuring SiO₂ NPs in H₂SO₄, 40 ppb of 100 nm SiO₂ NPs were added to 98% H₂SO₄ (shown as 0 h on the stability plot). The solution was then diluted 200x with UPW at around 1-hour intervals before measurement using the 8900 spICP-QQQ method. Figure 5 shows the stability of particle concentration and particle mean size for the 100 nm SiO₂ NPs in 200x H₂SO₄ over 10 hours. Both the particle concentration and size were constant over the long run, demonstrating the stability of the spICP-QQQ method.

The stability test also confirms the insolubility of SiO₂ NPs even in 98% H₂SO₄. Any SiO₂ NPs present in reagents such as H₂SO₄ could affect the production yield and/or performance of semiconductor devices.

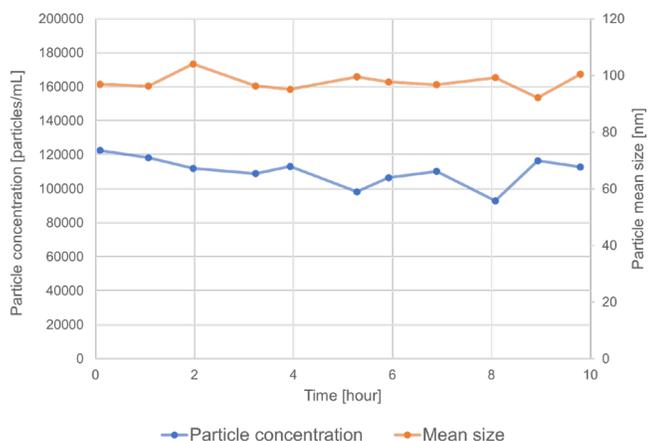


Figure 5. Long-term stability of particle concentration and particle mean size for 100 nm SiO₂ NPs in 200x diluted H₂SO₄.

SiO₂ NP analysis in IPA

The measurement of SiO₂ NPs in organic solvents by spICP-MS is challenging due to the formation of a ¹²C¹⁶O ion interference on ²⁸Si arising from the carbon matrix. The effectiveness of the spICP-QQQ method using MS/MS mode and H₂ cell gas to eliminate the CO interference on Si was tested by spiking undiluted IPA with 50 ppt of 60 nm SiO₂ NPs.

Figure 6 shows the signal distribution (left) and particle size distribution (right) of the 60 nm SiO₂ NPs in IPA. The 60 nm SiO₂ NPs were detectable in undiluted IPA using the spICP-QQQ method due to the high sensitivity and effective interference removal performance of the 8900 ICP-QQQ.

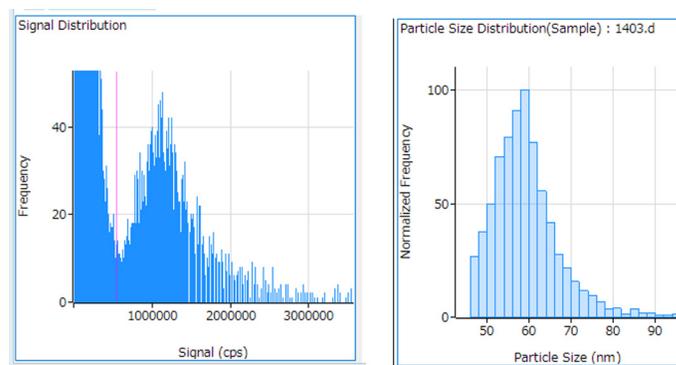


Figure 6. Signal distribution (left) and particle size distribution (right) of 60 nm SiO₂ NPs in undiluted IPA.

Conclusion

SiO₂ nanoparticles were determined and characterized in semiconductor grade HCl, H₂SO₄, and IPA by the Agilent 8900 ICP-QQQ operating in splCP-MS mode. Using H₂ in the ORS⁴ cell, MS/MS effectively eliminated N₂⁺ and CO⁺ polyatomic ion interferences on Si at *m/z* 28. The effective interference removal performance of the 8900 ICP-QQQ combined with its high sensitivity, enabled the detection of peaks from 50 or 60 nm particles above the background in all three ultrapure grade reagents.

The dedicated Single Nanoparticle Application Module for ICP-MS MassHunter software was used to calculate the particle sizes and concentration, providing good recoveries for the measurement of spiked NP samples during different tests:

- The sensitivity of the method was shown by the excellent recovery of the 20 ppt spike of 50 nm SiO₂ NPs in 7.2% HCl.
- Detection of 60 nm particles in undiluted IPA demonstrated the successful removal of the ¹²C¹⁶O⁺ interference on ²⁸Si arising from the organic matrix, as well as the ¹⁴N₂⁺ interference at *m/z* 28.
- The splCP-QQQ method was stable during a 10-hour study of 100 nm SiO₂ particles in 200x diluted H₂SO₄.

The 8900 delivered the low background, sensitivity, and spectral interference removal necessary for the analysis of 50 to 60 nm NPs in semiconductor grade acids and solvents.

The application is expected to become an increasingly important QC procedure for reagents used in the fabrication of high-performance devices.

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