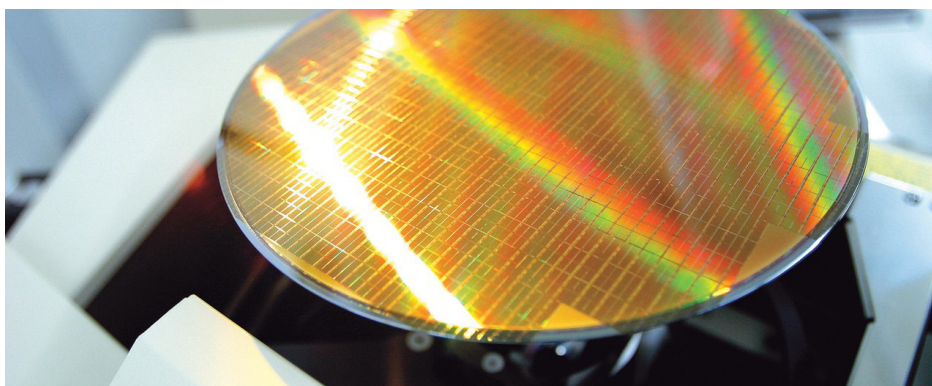**Agilent**

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Analysis of Nanoparticles in Organic Reagents by Agilent 8900 ICP-QQQ in spICP-MS Mode

Determination of 25 and 30 nm Fe_3O_4 NPs in low-particle concentration solutions

Author

Donna Hsu, Yoshinori Shimamura, Brian Liao, and Michiko Yamanaka[1]

Chun-Hua Chen and Chiu-Hun Su[2]

Ching Heng Hsu[3]

[1]Agilent Technologies, Inc.

[2]Industrial Technology Research Institute of Taiwan, Taiwan

[3]BASF Taiwan Ltd., Taiwan

Introduction

Semiconductor device manufacturing involves several processes including lithography, etching, ion implantation, and peeling. Even small amounts of impurities present in processing reagents such as developer, rinse solution, and etching liquid can cause defects, resulting in a reduction of product yield and degradation of product reliability. Metallic nanoparticles (NPs), especially iron (Fe) NPs, can lead to the occurrence of 'cone defects' on the surface of wafers, which cause shorting of electrical signals (1). To prevent these problems from arising, an accurate analytical method is required to determine metallic NPs in semiconductor process chemicals.

Single particle ICP-MS (spICP-MS) is a powerful tool that is used increasingly to characterize the NP content of various types of samples (2–4). spICP-MS allows the simultaneous determination of the number, concentration, and size of particles, plus the dissolved element concentration. It can be applied to the measurement of semiconductor grade organic solvents such as isopropyl alcohol (IPA), propylene

glycol methyl ether acetate (PGMEA), and butyl acetate (BuAc), as well as aqueous solutions (*3*). To detect very small-sized NPs using spICP-MS, an instrument with a low background and high sensitivity such as the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) is needed. Also, since some metallic NPs suffer from spectral interferences, the advanced interference removal capability of the 8900 ICP-QQQ is advantageous for the application.

In this study, Fe NPs were measured in semiconductor grade IPA, PGMEA, and BuAc using the Agilent 8900 ICP-QQQ operating in spICP-MS mode.

Experimental

Sample preparation

Two kinds of Fe_3O_4 NP (Fe NP) solutions, 25 nm (Sigma Aldrich, p/n 900027) and 30 nm (Sigma Aldrich, p/n 747408), were used as NP standards. The Fe NPs were spiked into IPA, PGMEA, and BuAc. These organic solvents were introduced directly to the ICP-QQQ. To measure the ionic sensitivity of Fe, an aqueous Fe standard (1000 ppm, Kanto Chemicals, Japan) was diluted with each organic solvent.

Instrumentation

An Agilent 8900 ICP-QQQ (#200, Semiconductor configuration) and Agilent SPS 4 autosampler were used for all measurements. The sample introduction system comprised a quartz torch with a 1.5 mm i.d. injector, quartz spray chamber, and platinum-tipped interface cones. The SPS 4 autosampler was fitted with a sample rack (produced in Taiwan) designed to accommodate larger sample bottles (100 to 500 mL). Being able to load the same bottles used for sample preparation into the SPS 4 rack reduces the risk of contamination as the samples don't need to be transferred to smaller bottles. Also, larger bottles are convenient for the long-term stability test. The samples were self-aspirated using an Agilent PFA nebulizer, which is part of the SPS 4 probe kit (p/n G3139-68000). Clean argon gas was purged into the cover of the autosampler and there was a constant flow of ultrapure water via a continuous flow rinse port fitted to the SPS 4.

The 8900 ICP-QQQ was operated in MS/MS mode for all Fe measurements. Both Q1 and Q2 (unit mass filters) were set to *m/z* 56. Q1 selects which elements enter the ORS[4] collision/reaction cell (CRC), allowing controlled reaction chemistry to take place in the cell when a reactive cell gas is introduced. Ammonia cell gas was used to control the ArO and C_2O_2 interferences that overlap Fe at *m/z* 56.

The signal generated by a single NP lasts for about 1 ms, so Fast Time Resolved Analysis (TRA) mode of the 8900 ICP-QQQ was used to acquire the data. Fast TRA allows single element acquisition at a sampling rate of 100 µs (10,000 measurements per second) and no settling time is needed

between measurements. Data analysis was performed using the Single Nanoparticle Application Module of the Agilent ICP-MS MassHunter software.

The operating conditions of the Agilent 8900 ICP-QQQ are detailed in Table 1. As shown, slightly different parameters were used to achieve optimum sensitivity for the determination of Fe NPs in each solvent. To enable the direct injection of organic solvents to the ICP-QQQ without the deposition of carbon on the cones, oxygen gas (20%, Ar balanced) was added to the sample gas flow.

Table 1. ICP-QQQ operating conditions.

Parameter	Value		
	IPA	PGMEA	BuAc
RF power (W)	1400	1500	1500
Sampling depth (mm)	18.0		
Nebulizer gas (L/min)	0.70		
Makeup gas (L/min)	0.50	0.60	0.45
*Option gas (L/min)	0.40 (40%)	0.20 (20%)	0.40 (40%)
Spray chamber temp. (°C)	2		
Extraction lens 1 (V)	−150	−125	−125
Extraction lens 2 (V)	−10	−15	−15
Octopole bias (V)	−10	−3	−3
Axial acceleration (V)	1.5		
Energy discrimination (V)	−10	−7	−7
He flow rate (mL/min)	1		
**NH_3 flow rate (mL/min)	2 (20%)	3 (30%)	3 (30%)
Dwell time (µs)	100		
Masses monitored	Fe (Q1: 56, Q2: 56)		
Data acquisition time (s)	60		

*20% O_2 balanced with Ar added using the option gas mass flow controller, which is fitted as standard on the Agilent 8900 Semiconductor ICP-QQQ. **10% NH_3 balanced with He.

Results and discussion

Analysis of Fe NPs in IPA, PGMEA, and BuAc

Solutions of IPA, PGMEA, and BuAc containing 30 nm Fe NPs spiked at 5 ppt were measured using the 8900 ICP-QQQ. The signal distribution and size distribution plots for Fe NPs in each of the samples are shown in Figure 1. The signals generated from the Fe NPs were clearly separated from the background signals. Also, the mean measured particle size was around 30 nm in all spiked solvents, which is consistent with the nominal Fe NP diameter (30 nm). The Single Nanoparticle Application Module software automatically sets the particle threshold, which is shown by the pink line in the signal distribution plots.
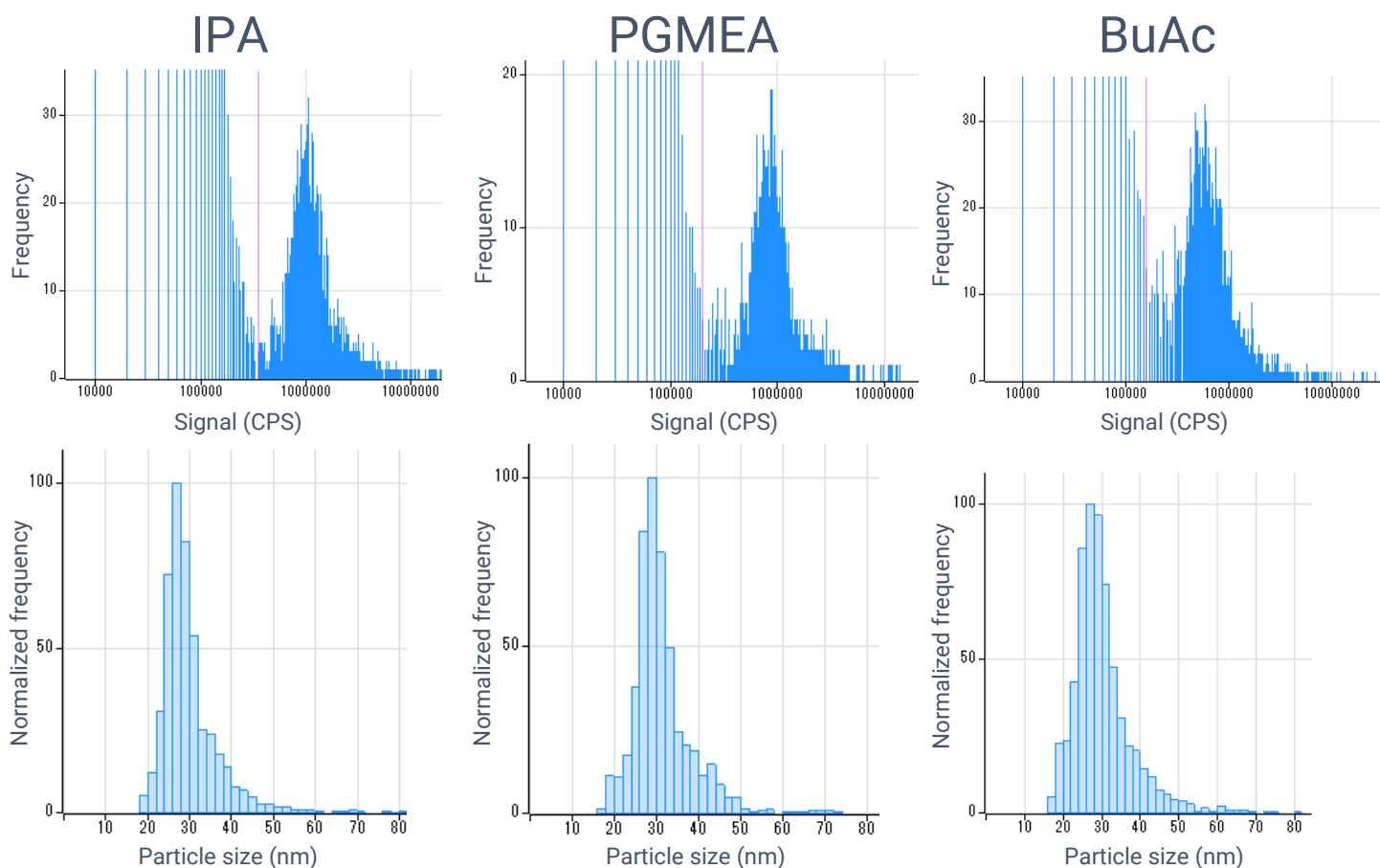
Figure 1. Signal distribution (upper) and size distribution (lower) of 30 nm Fe NPs in solutions of IPA, PGMEA, and BuAc.

The spICP-MS software automatically calculates the nebulization efficiency, which is the ratio of the amount of analyte entering the plasma to the amount of analyte delivered to the nebulizer. By measuring 30 nm Fe NP, the nebulization efficiency (calculated by size) was found to be around 0.30 (30%) for all three organic solvents. The sensitivity of ionic Fe ranged from 1500 cps/ppt to 2400 cps/ppt depending on the solvent. The background equivalent concentration (BED) of the blank reagents was around 6 nm.

Linearity of detected particle number concentration in terms of spiked concentration

Figure 2 shows the size distribution of 25 nm Fe NPs dispersed in IPA solution at several concentrations (0, 0.1, 0.5, 1, and 2 ppt). The graph clearly indicates a Gaussian distribution for 0.5, 1, and 2 ppt of Fe NPs. It wasn't possible to detect NPs smaller than 18 nm due to the background signal from the small amount of ionic Fe present in the sample (BEC = 0.6 ppt).
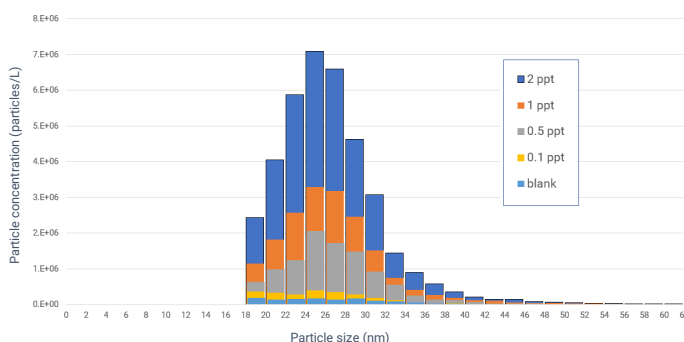

Figure 2. Size distribution data for 25 nm Fe NPs spiked at 0, 0.1, 0.5, 1, and 2 ppt in IPA. The vertical axis shows the particle number concentration for each range of particle sizes (each bar represents a size range of 2 nm).

Figure 3 shows the relationship of measured particle number concentration (particle/L) against the spiked concentration of Fe NPs in IPA. Almost perfect linearity ($R^2 = 0.998$) was obtained across the concentration range of 0.1 to 2 ppt. These results show that 25 nm Fe NPs can be determined in IPA solutions containing very low concentrations of Fe NPs using the 8900 ICP-QQQ operating in spICP-MS mode.
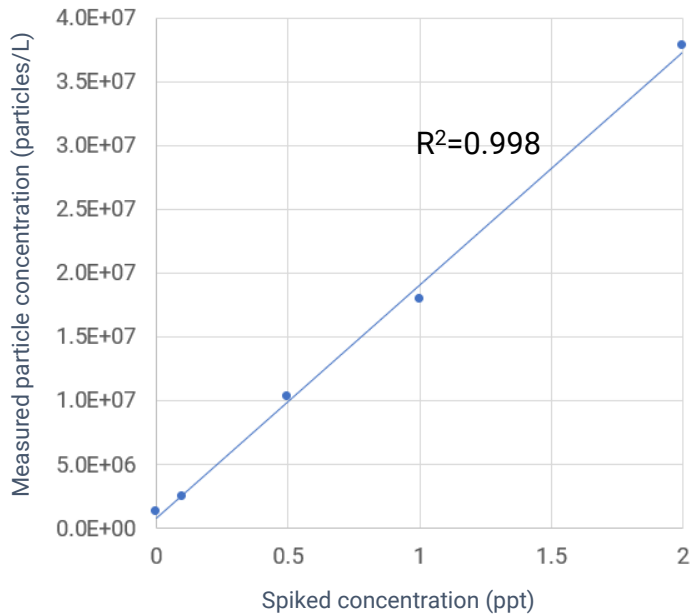

Figure 3. Relationship between the spiked concentration of 25 nm Fe NPs and measured particle number concentration in IPA.

Long-term stability test

Figure 4 shows the stability of detected particle number (representing particle number concentration) and particle size for 30 nm Fe NPs in the three solvents over 12 hours. Both the detected particle number and the size were constant over 12 hours, as indicated by the %RSDs. The stability of Fe NPs in each solvent means they can be measured accurately, even a long time after sample preparation.

Conclusion

Using an spICP-MS method, the Agilent 8900 ICP-QQQ operating in MS/MS mode was used for the determination and characterization of iron-based nanoparticles in IPA, PGMEA, and BuAc.

Standards containing 25 or 30 nm Fe_3O_4 nanoparticles were spiked into the organic solvents and the particle size and the particle number concentration were determined using the spICP-MS method. The small-sized particles were successfully measured in solutions with a particle concentration ranging from 0.1 to 2 ppt. Also, the particle size and particle concentration of Fe NPs were stable in each of the three organic solvents over 12 hours.

Overall, the method delivered the low background, sensitivity, and spectral interference removal necessary for the analysis of small-sized NPs in semiconductor grade organic solvents.
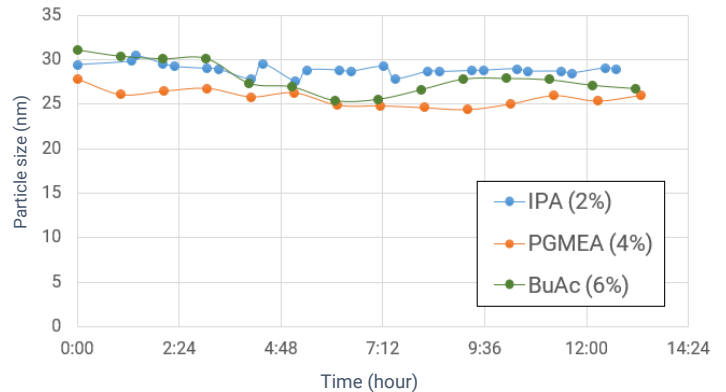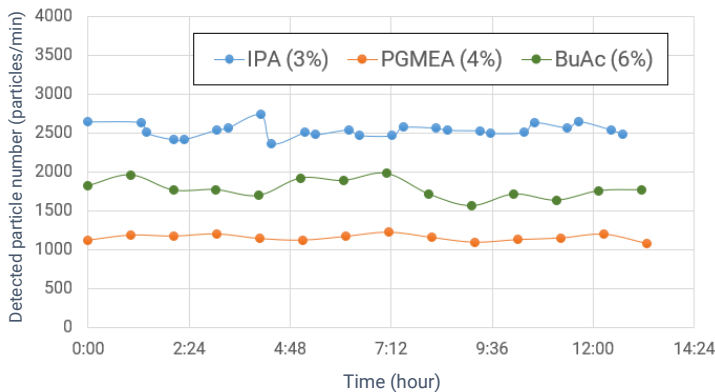

Figure 4. Long-term stability of 30 nm Fe NPs in IPA, PGMEA, and BuAc over 12 hours. The left graph shows the detected particle number and the right graph shows the average particle size. The numbers in parentheses are RSD%.

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