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Using ICP-MS/MS with M-Lens for the analysis of high silicon matrix samples

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Introduction

The expansion of the connected devices and the Internet of Things (IoT) has resulted in semiconductor processing facilities (known as an Integrated Circuit Foundry) to increase production to meet the requirements of this rapidly expanding market. As IC Foundries turn silicon wafers into integrated circuits, the determination and control of trace metal impurities in a high silicon matrix has become crucial in the manufacturing process.

Single quadrupole ICP-MS is the most widely used atomic spectrometry technique for the measurement of trace elements but with advanced semiconductor processes requiring elemental impurities on the silicon wafer to be 1.0^{E+7} atom/cm^2 level, it can be difficult to meet these specifications.

The development of triple quadrupole ICP-MS with MS/MS capabilities that can selectively remove interferences caused by silicon, as well as many other interferences, has greatly enhanced the obtainable detection limits (DLs) to less than 1ppt.

Another critical issue encountered in this analysis is the high silicon matrix can cause severe suppression of analytes and silicon deposition, which impacts the stability of the measurement. To address the sensitivity suppression caused by the silicon matrix as well as the need for improved stability in this matrix, a new lens (M-lens) was developed. The new M-lens was designed with the high purity chemical market in mind, allowing sub-ppt BEC of Na, K, and Ca in hot plasma conditions (CeO^+/Ce^+ <1.5%) as well as improved stability in difficult matrixes.

In this study, using an ICP-MS/MS with the M-lens, we investigated two kinds of common silicon matrix samples used in the semiconductor industry.

Experimental

Instrumentation

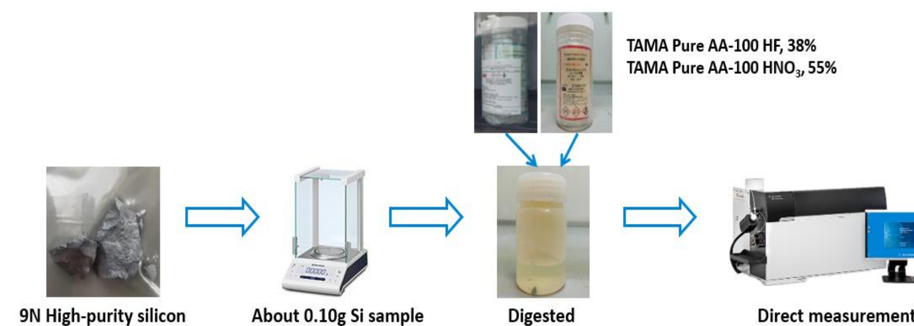
An Agilent 8900 ICP-MS/MS was used for this study. The configuration of the instrument included helium, hydrogen, oxygen and ammonium as collision/reaction gases used to remove the polyatomic interferences. The M-lens was also used for its high silicon matrix tolerance and ability to achieve excellent measurement stability in difficult samples.

Experimental

Sample preparation

Electrotonic grade silicon of 9N purity was used as the base material. Trace-level of nitric acid (TAMAPure AA-100, Kanagawa, Japan) and hydrofluoric acid (TAMAPure AA-100, Kanagawa, Japan) were used as the reagents to produce high silicon matrix samples.

The sample preparation followed was to weigh the electrotonic grade silicon to the nearest 0.05g, clean the surface with HNO_3 and ultrapure water, then digest the silicon with 38% HF and 55% HNO_3 1:1 (w/w) mix acid to the nearest 50.0g. Dilute this 1000ppm Si matrix solution to get two typical high silicon matrix samples: 10ppm Si for the concentration of typical bare wafer; 100ppm Si for poly-Si after sample preparation.



ICP-MS/MS Operating Parameters

The operating parameters of the Agilent 8900 Triple Quadrupole ICP-MS/MS for advanced applications was used along with a 200µL/min PFA MicroFlow nebulizer and 2.5mm sapphire injector and inert torch. Three modes (all hot plasma) were used in this study.

Table 1. Operating parameters of ICP-MS/MS

Parameter	Value	Parameter	Value
RF (W)	1550	Spray chamber temp. (℃)	2
Sampling depth (mm)	8.0	He flow rate (mL/min)	4.5
Carrier gas (L/min)	0.8	H_2 flow rate (mL/min)	10.0
Makeup gas (L/min)	0.4	NH_3 flow rate (mL/min)	2.0
Integration time (s)	0.6		

Spectral interferences

Possible spectral interferences caused by high level silicon in samples, are listed in Table 2.

Table 2. Spectral interferences caused by silicon matrix

Analyte ion	Interferences	Analyte ion	Interferences
$^{46}Ti^+$	$^{30}Si^{16}O^+$	$^{58}Ni^+$	$^{28}Si^{30}Si^+$ $^{29}Si^{29}Si^+$
$^{47}Ti^+$	$^{28}Si^{19}F^+$ $^{30}Si^{16}OH^+$	$^{60}Ni^+$	$^{28}Si^{16}O_2^+$ $^{30}Si^{30}Si^+$
$^{48}Ti^+$	$^{28}Si^{19}F^+$ $^{30}Si^{18}O^+$	$^{63}Cu^+$	$^{28}Si^{16}O^{19}F^+$
$^{49}Ti^+$	$^{30}Si^{19}F^+$	$^{65}Cu^+$	$^{30}Si^{16}O^{19}F^+$ $^{28}Si^{18}O^{19}F^+$
$^{56}Fe^+$	$^{28}Si^{28}Si^+$		

To obtain ppt level DLs, spectral interferences are removed by the use of ammonium as a reaction gas. In the example below, we take ^{48}Ti and share how ICP-MS/MS removes the interferences in mass-shift mode, as shown in Fig.1.

Figure 1. Mechanism of MS/MS mass-shift mode, using NH_3 for the measurement of ^{48}Ti

The SiF^+ and SiO^+ interferences on ^{48}Ti were removed by NH_3 mass-shift mode. This is possible as in the reaction cell, the analyte ion $^{48}Ti^+$ combines with the reaction gas NH_3 to form the "new" analyte ion $TiNH(NH_3)_3^+$, while the interference ions (SiF^+ and SiO^+) do not react with NH_3. In Q2, only ions of mass m/z=114 $TiNH(NH_3)_3^+$ are transmitted to the detector, while interference ions (SiF^+ and SiO^+) are removed and do not contribute to the signal at the "new" analyte ion.

In order to ensure the spectral interferences were being properly removed by the MS/MS reaction mechanism, results of different masses of the same element (^{58}Ni & ^{60}Ni, ^{63}Cu & ^{65}Cu) were evaluated to determine the effectiveness of MS/MS. The results of a 100ppm Si matrix sample measurement is shown in Fig. 2.

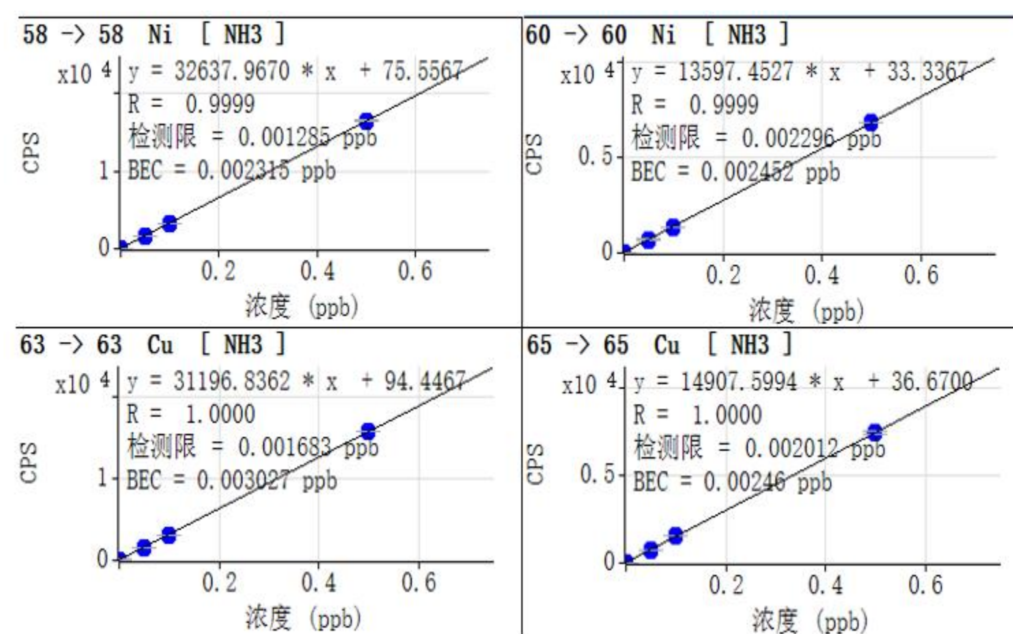


Figure 2. Measurement result of ^{58}Ni & ^{60}Ni, ^{63}Cu & ^{65}Cu

From the results shown in Fig. 2, the BEC (Background Equivalent Concentration) of different mass are in very good agreement which indicates that MS/MS mass-shift mode is effective at removing the spectral interferences.

The robust performance of ICP-QQQ with MS/MS mode is effective at removing the Si interferences, allowing ppt level analysis in the high silicon matrix. The BECs of all 38 analyte ions are lower than 50ng/L in both 10ppm &100ppm Si matrix samples. Also, the achieved DLs of all elements are at the ppt level.

Stability of measurement

To test both the stability of the specially designed M-Lens and the robustness of the MS/MS reaction mechanism with the high silicon matrix, a standard solution of 50ng/L was spiked in the prepared 10ppm & 100ppm Si matrix samples. Each sample had 11 replicate measurements performed and the analysis was carried out over a 1h time period. The results are shown in Table 3.

PFA Sample Introduction System **M-Lens**

Results and Discussion

Table 3. Analysis stability result of 10ppm & 100ppm silicon matrix samples

	10ppm Si			100ppm Si		
Analyte ion	Spike Average (ug/L)	RSD	Recovery	Spike Average (ug/L)	RSD	Recovery
Li	0.051	3.7%	101.40%	0.053	3.4%	107.27%
Be	0.050	3.6%	99.36%	0.053	4.7%	105.66%
B	0.053	4.0%	105.94%	0.055	3.2%	109.68%
Na	0.051	5.6%	101.84%	0.049	2.9%	96.71%
Mg	0.047	3.0%	93.92%	0.054	4.4%	108.20%
Al	0.051	3.8%	103.12%	0.048	2.2%	97.67%
K	0.047	2.3%	93.56%	0.053	2.6%	105.11%
Ca	0.048	2.1%	95.77%	0.054	3.3%	108.88%
Ti	0.051	5.6%	101.28%	0.050	5.1%	101.68%
V	0.045	2.5%	90.80%	0.051	4.6%	102.28%
Cr	0.048	2.5%	95.86%	0.050	2.8%	101.42%
Mn	0.052	3.8%	103.76%	0.048	1.5%	96.20%
Fe	0.056	6.0%	112.01%	0.053	3.9%	106.90%
Co	0.045	2.4%	90.02%	0.049	3.2%	99.11%
Ni	0.046	4.0%	92.23%	0.048	2.3%	96.74%
Cu	0.050	5.6%	99.39%	0.047	5.9%	94.48%
Zn	0.051	5.1%	101.08%	0.047	5.7%	95.69%
Ga	0.048	2.4%	94.84%	0.055	2.8%	109.81%
Ge	0.046	2.0%	90.68%	0.049	1.7%	98.05%
As	0.045	4.7%	90.27%	0.050	5.9%	100.41%
Nb	0.045	5.0%	90.38%	0.048	4.5%	97.19%
Mo	0.048	2.0%	96.48%	0.051	4.5%	100.58%
Ag	0.048	2.0%	95.30%	0.051	2.5%	101.23%
Se	0.048	1.9%	94.93%	0.051	2.3%	102.23%
Rb	0.046	2.6%	91.48%	0.049	2.7%	98.20%
Sr	0.047	2.9%	93.81%	0.049	4.3%	98.03%
Zr	0.049	1.9%	98.17%	0.051	1.6%	100.77%
Cd	0.048	1.7%	95.85%	0.049	2.5%	98.07%
Sn	0.048	2.5%	96.68%	0.049	2.1%	97.55%
Sb	0.047	2.3%	93.93%	0.048	2.6%	95.25%
Cs	0.047	2.7%	94.61%	0.049	1.8%	97.01%
Ba	0.049	2.3%	97.55%	0.050	1.9%	98.43%
Ta	0.050	2.2%	98.84%	0.048	1.6%	96.40%
W	0.050	4.2%	99.19%	0.048	2.2%	96.13%
Re	0.048	2.9%	95.82%	0.048	1.9%	95.91%
Tl	0.052	3.0%	104.21%	0.052	1.3%	103.17%
Pb	0.049	2.2%	98.01%	0.048	1.9%	96.07%
U	0.052	3.3%	103.15%	0.051	1.0%	101.20%

The data shows good RSD's (<6%) across all 38 elements for both the 10ppm silicon and the 100ppm silicon matrixes.

This confirms that the M-lens greatly reduces signal suppression and offers excellent robustness and sensitivity as spike recoveries in both silicon matrixes ranged from 90% to 110%, except iron (Fe) in 10ppm silicon sample. The slightly high Fe result was likely the result of environmental contamination during the 1h analysis time.

Conclusions

8900 ICP-MS/MS with M-lens: effective analysis solution of high silicon matrix samples

- ICP-MS/MS operated in tandem MS/MS mode using NH3 as a reaction gas is effective at controlling the reaction process and preventing unwanted ions from contributing to elevated BEC's and DL's.
- M-Lens can reduce the impact on signal suppression caused by high silicon deposition and improve measurement stability
- 8900 ICP-MS\MS can completely remove the spectral interferences caused by high sample matrixes while offering ultra-trace analysis to meet the specifications of the most advanced IC manufacturing process.

References

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