Determination of Trace Metal Impurities in Semiconductor-Grade Hydrofluoric Acid

Application

Semiconductor

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Abstract

This application note describes the analysis of metallic impurities in semiconductor-grade hydrofluoric acid by inductively coupled plasma mass spectrometry (ICP-MS). The Agilent 7500s ICP-MS instrument with its ShieldTorch technology was used to analyze 38% (w/w) hydrofluoric acid directly for all of the elements commonly required by the semiconductor industry. Combined with the high-sensitivity characteristic of the ShieldTorch System, the off-axis ion lens assembly in the Agilent 7500s provided excellent signal/background resulting in exceptional detection limits for all elements (0.02- to 5-ppt range). Excellent spike recovery data at the 5-ppt level further highlights the suitability and accuracy of the Agilent 7500s for the determination of all Semiconductor Equipment and Materials International (SEMI) required elements in hydrofluoric acid at ultra-trace levels.

Introduction

The semiconductor industry uses solutions of hydrofluoric (HF) acid for wet chemical cleaning or etching of silicon dioxide on silicon wafers and integrated circuits (ICs) during the manufacturing process. These cleaning processes usually involve immersion into etching baths containing dilute hydrofluoric acid. It is critical during the cleaning process that these chemical etching baths do not contaminate the wafer surface and ICs. Metallic contaminants in semiconductor devices can diffuse on the surface, diffuse into the device itself, and accumulate at interfaces. This results in surface conduction that decreases minority carrier lifetime, degrades electrical device performance, and lowers product yield. In fact, over 50 percent of the yield losses in IC manufacturing are caused by micro-contamination[1]. To minimize this risk, many incoming chemicals are analyzed for their chemical purity and the etching baths are sampled regularly during their useful lifetimes.

This application note describes the use of an Agilent 7500 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) system, fitted with an HF-resistant sample introduction system, to analyze semiconductor-grade HF (38% w/w) with excellent recoveries (75 to 125%) for a 5-ppt spike added directly to the concentrated acid.

Recent advances in ICP-MS and sample introduction technology allow the routine, direct assay of

38% (w/w) HF for all Semiconductor Equipment and Materials International (SEMI) required elements, including K, Ca, Fe and Zn, at single ppt levels. The chemically inert, O-ring-free perfluoroalkoxyalkane (PFA) sample introduction system allows direct, contamination-free introduction of the concentrated acid into the ICP-MS. The combination of a PFA microflow nebulizer, Peltier-cooled spray chamber, and robust 27-MHz plasma ensure complete matrix decomposition and ionization of the sample including difficult elements such as boron and zinc, which have high ionization potentials. This eliminates the need for the use of internal standards, thereby eliminating a potential source of contamination. Matrix-based interferences on key elements, such as Ca, K, and Fe, were virtually eliminated using cool plasma conditions and Agilent Technologies' exclusive ShieldTorch Technology. In addition, the unique Omega II ion lens system in the Agilent 7500s ICP-MS results in a 10- to 100-fold enhancement in the signal-to-background (S/B) ratio for elements across the entire mass range.

Switching between operating modes is automated using Agilent's Multi-Tune software functionality and requires that each autosampler vial be sampled only once, thereby minimizing any potential for sample contamination. Analytical results are collated and presented in a single report. Normal/Cool plasma switching has proven to be rapid and stable over extended periods of operation resulting in the excellent S/B, signal stability, and detection capability required for this analysis[2].

Experimental

Instrumentation

The instrument used in this application was an Agilent 7500s ICP-MS equipped with the ShieldTorch System (STS) and an HF-resistant, PFA sample introduction system (Elemental Scientific, Omaha NE, USA). The Elemental Scientific PFA sample introduction system (part number ES-2161-7500) consists of a PFA-100 high efficiency, self-aspirating micro flow nebulizer, 35 mm PFA PureCap end cap, 35 mm PFA spray chamber, 2-mm O-ring free Pt injector and precision quartz torch.

The Agilent 7500s was operated in "soft extraction" mode[3,4]. In this mode of operation, a slight positive voltage is applied to the first lens of the 7500s' twin extraction lenses. This automated optimization procedure dramatically reduces the background across the entire mass range without any sacrifice in sensitivity. The result is a 10- to 100-fold increase in the S/B ratio for most elements.

Potentially troublesome argon polyatomic ions on key elements, like K, Ca, Fe, Ge, V, and Zn, were virtually eliminated using Agilent's STS combined with cool plasma operating conditions. Unlike traditional cool plasma conditions, which require plasma powers of 500 to 550 W, the Agilent 7500s is able to effectively eliminate argon based polyatomic interferences while operating at higher, more robust plasma conditions. In addition, the STS is highly efficient at reducing the plasma potential to approximately 1 eV, significantly lower than with non-shield plasma locking devices. This leads to better ion focusing and more efficient interference removal, thereby alleviating the need for sample pretreatment or complex scanning reaction/collision cell technologies.

Sample Preparation

All sample analysis was performed directly without any preparation or pretreatment, which avoids contamination and leads to improved detection limits. Analyses were performed using the method of standard additions (MSA) on an ultrapure-grade HF sample. Calibration curves were prepared at concentrations ranging from 0.5 to 10 ng/L (ppt). A single MSA curve was established and converted into an external calibration curve, thereby eliminating the need to spike each subsequent sample to be analyzed. Once an external calibration curve has been established from the MSA curve in this manner, all other sample concentrations can be determined against it. No internal standards were used in this study to minimize the risk of sample contamination. Following quantitation, HF samples were spiked at a level of 5 ppt (ng/L) to assess the accuracy of the measurement. All sample handling and data analysis was performed under Class 100 cleanroom conditions.

Table 1. ICP-MS Operating Conditions

Parameter	Cool plasma conditions	Normal plasma conditions
RF power	630 W	1300 W
Sampling depth	18.5 mm	7 mm
Carrier gas flow	0.9 L/min	0.94 L/min
Makeup gas flow	1.0 L/min	0.1 L/min
Extraction lens 1	- 80 V	+ 4.7 V
Extraction lens 2	- 20 V	- 5 V

ICP-MS Analysis

The sample was self-aspirated at an uptake rate of 100 µL/min. Instrument operating conditions are given in Table 1.

Switching between normal and cool plasma conditions is fully automated using Agilent's Multi-tune software. Multi-tune allows complete data collection in a single acquisition, with a single visit to the sample vial, thereby saving time and reducing the potential for sample contamination. In addition, all resulting data is compiled in a single report. Stabilization time in switching between plasma operating modes is minimal at 20 seconds. The stability of switching between operating modes over prolonged periods was previously demonstrated to be 3% RSD over an 8-hour period[2].

Results and Discussion

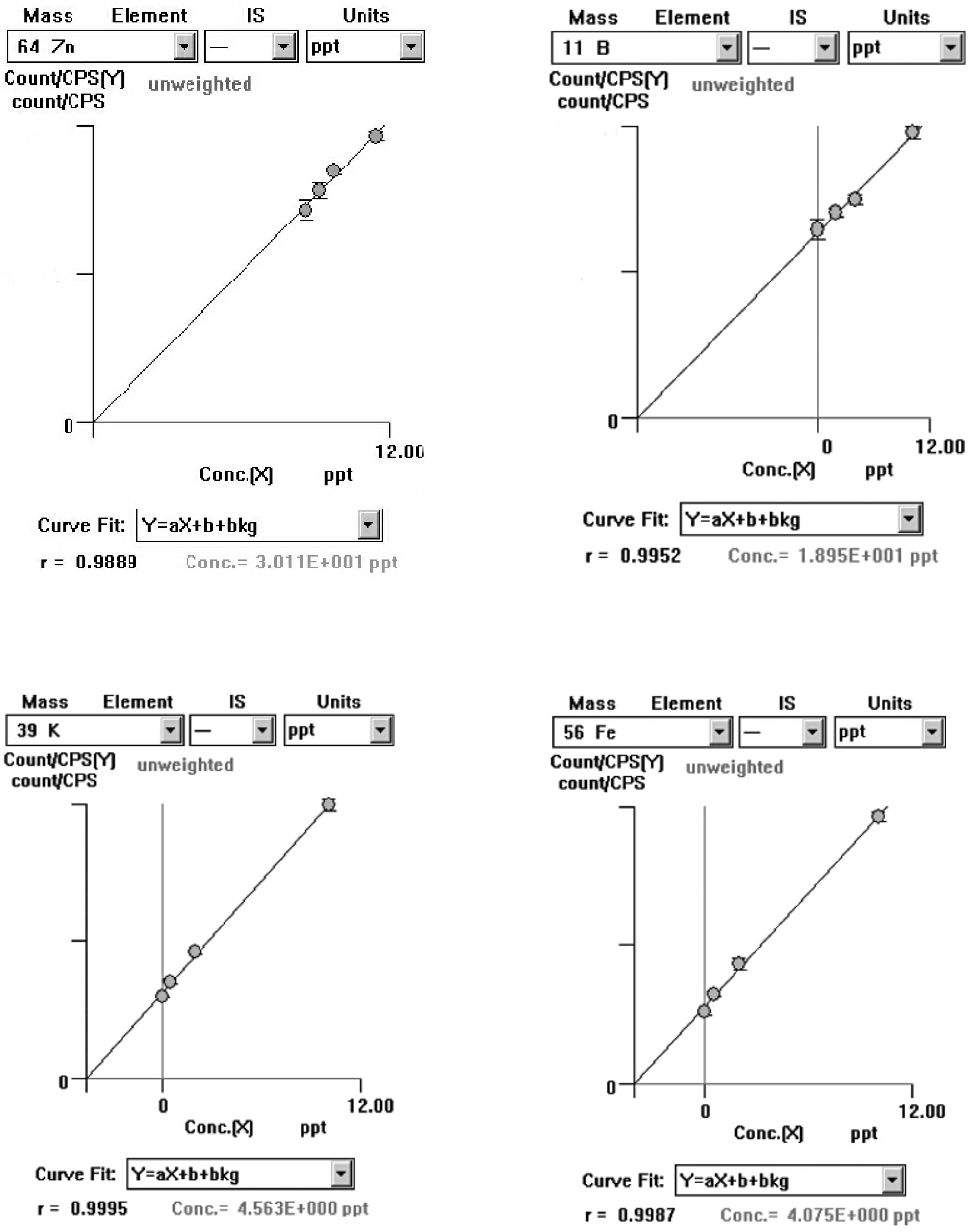
The results in Table 2 show detection limits (ppt) and spike recovery data for a standard suite of semiconductor elements in undiluted HF. Note the exceptional performance even for more difficult elements such as Ca, K, and Fe.

Table 2. Detection Limits (Parts-Per-Trillion) and Spike Recoveries (%) in Undiluted HF (38%)

Element	Mass	7500 DL (ppt)	Blank conc (ppt)	Blank plus 5 ppt	Percent recovery	Plasma mode
Li	7	0.05	0.0	5.0	99	Cool
Be	9	0.2	0.1	5.0	100	Normal
B	11	3	19.2	24.4	103	Normal
Na	23	0.09	2.5	7.6	102	Cool
Mg	24	0.1	0.6	5.8	105	Cool
Al	27	0.2	2.0	7.8	117	Cool
K	39	0.1	4.4	9.8	108	Cool
Ca	40	2	21.7	26.6	98	Cool
Ti	48	5	76.8	81.7	98	Normal
V	51	3	42.6	48.1	112	Normal
Cr	52	1	13.0	18.2	104	Cool
Mn	55	0.2	1.4	6.3	99	Cool
Fe	56	0.3	3.8	9.3	111	Cool
Ni	58	0.1	0.1	5.1	102	Cool
Co	59	0.2	0.5	5.7	104	Cool
Cu	63	0.3	0.6	5.6	100	Cool
Zn	68	0.8	2.2	6.4	83	Cool
Ga	69	0.05	0.1	4.9	97	Cool
Ge	74	5	52.2	56.2	79	Normal
Rb	85	0.02	0.0	5.1	102	Cool
Sr	88	0.1	0.1	5.3	103	Cool
Zr	91	4	26.2	31.4	103	Normal
Nb	93	0.5	2.3	7.2	96	Normal
Mo	98	2	37.4	41.7	85	Normal
Ag	107	0.08	0.2	4.9	95	Cool
Cd	114	0.5	6.8	12.0	104	Normal
Sn	118	0.2	1.2	5.8	93	Normal
Sb	121	1	7.0	12.3	107	Normal
Ba	138	0.06	0.2	4.8	93	Normal
Ta	181	0.1	1.8	6.6	97	Normal
W	182	0.9	4.4	9.8	107	Normal
Au	197	0.2	0.2	5.1	96	Normal
Tl	205	0.08	0.1	5.1	100	Normal
Pb	208	0.08	0.2	5.1	98	Normal
Bi	209	0.05	0.1	4.9	96	Normal
U	238	0.02	0.0	4.7	93	Normal

Representative calibration curves are given in Figure 1. Excellent correlation coefficients were obtained considering the low concentration levels used. The good fit at the single ppt level on each calibration curve shows this level of analyte can be reliably quantified in undiluted HF.

Detection limits were calculated using three times the standard deviation (n = 3) of the raw counts of the HF blank divided by the slope of the calibration curve. The reported detection limits are generally excellent and are dependent upon the trace metal content in the blank. This provides opportunity for even further improvement upon the reported values. All detection limits are in the range 0.02 to 5 ppt (ng/L) in the 38% HF.



Mass: 64 Zn, IS: —, Units: ppt
Curve Fit: Y=aX+b+bkg
r = 0.9889 Conc.= 3.011E+001 ppt

Mass: 11 B, IS: —, Units: ppt
Curve Fit: Y=aX+b+bkg
r = 0.9952 Conc.= 1.895E+001 ppt

Mass: 39 K, IS: —, Units: ppt
Curve Fit: Y=aX+b+bkg
r = 0.9995 Conc.= 4.563E+000 ppt

Mass: 56 Fe, IS: —, Units: ppt
Curve Fit: Y=aX+b+bkg
r = 0.9987 Conc.= 4.075E+000 ppt

Figure 1. Representative calibration curves for B and Zn obtained using the method of standard addition (Blank, 2, 4 and 10 ppt) and K and Fe (Blank, 0.5, 2 and 10 ppt).

A 2-hour stability study was performed by adding a 10-ppt standard to the 38% HF and analyzing the spiked sample over a 2-hour period. Instrument stability over this period was excellent with %RSD values typically less than 3% over the period. Figure 2 is a stability plot of representative elements.

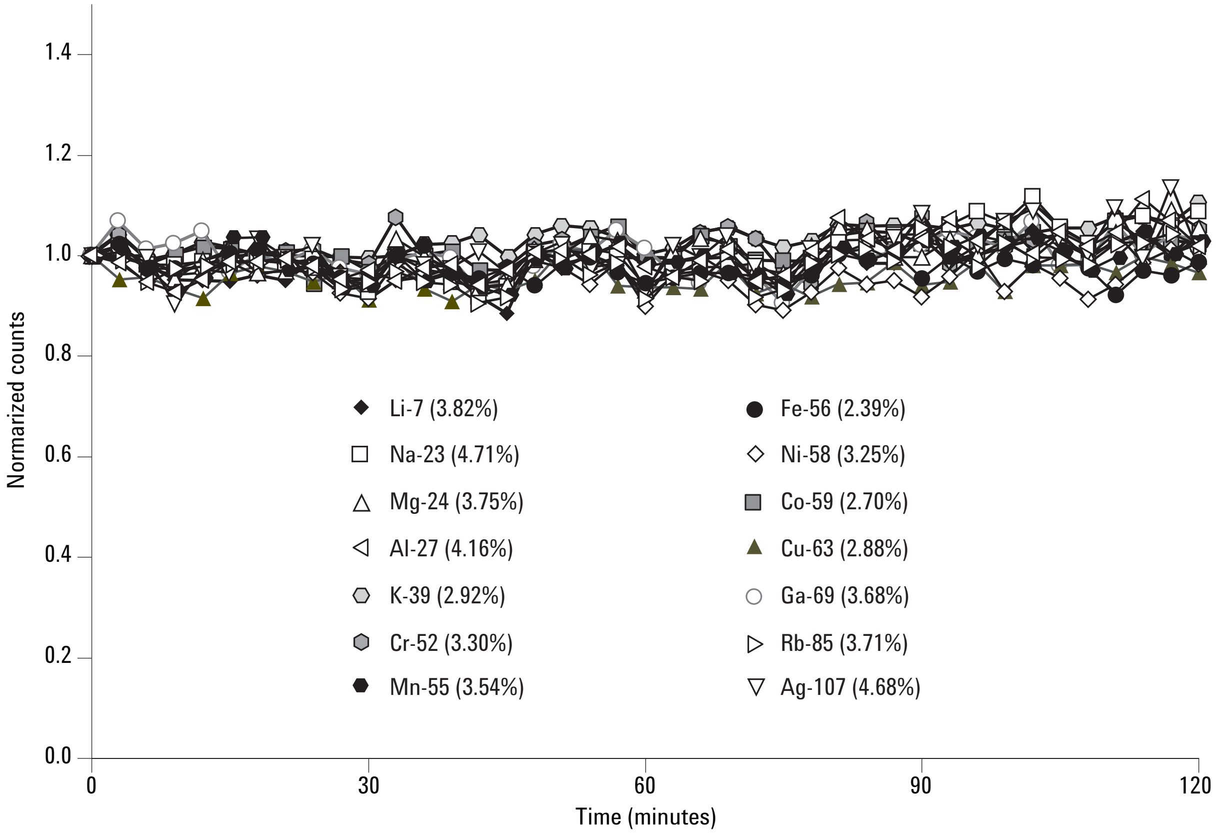


Figure 2. Analysis of 10 ppt multi-element standard spiked into 38% HF measured repeatedly over a 2-hour period.

Conclusions

Direct analysis of concentrated hydrofluoric acid (38% w/w) at the 5-ppt level is possible using the Agilent 7500s with ShieldTorch System and a trace metal-free, high-efficiency, inert sample introduction kit (Elemental Scientific, Omaha, NE). As is often the case when making ultra-trace measurements, analytical results are highly dependent upon laboratory environment and analytical methodology. In this study, all data was obtained under cleanroom conditions with minimal sample handling. The excellent detection limits and spike recovery data highlight the suitability and accuracy of the Agilent 7500s ICP-MS to determine low ppt level impurities in the concentrated acid even for difficult elements like B, Zn, K, Ca and Fe. The robust 27-MHz plasma ensures complete sample decomposition providing plasma stability when operating in cool plasma mode as well as ionization of elements with a high ionization potential, such as boron and zinc. The patented ShieldTorch System enhances system sensitivity while reducing the spectral interferences on key elements while the dual extraction lenses and off-axis Omega lens system reduce the S/B by a factor of 100. The result is uncompromised quantification at the low ppt level without the need for sample pretreatment or complex scanning reaction/collision cell technologies.

Samples were analyzed using the MSA. Only the first sample is spiked with the calibration standards. The MSA regression generated from the first sample is then converted to an external calibration curve, eliminating the need to spike all subsequent samples. This protocol enhances sample throughput while eliminating potential sources of contamination. Finally, Agilent's Multi-mode software ensures walk-away automation even when changing instrument operating modes. All data is collected in a single acquisition, with a single visit to the sample vial, and presented to the user in a single report.

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