APPLICATION BRIEF

ICP - Mass Spectrometry

Authors:

Chung Ryu
Sooyoung Yoon

PerkinElmer, Inc.
Seoul, Korea

Ultra-Trace Quantification of Non-Metals in Sulfuric Acid Solutions Using the NexION 5000 ICP-MS Under Different Cell Gas Conditions

Introduction

As semiconductor manufacturing processes are being performed at increasing micro-levels, there has been a growing demand for ICP-MS instrumentation capable of analyzing non-metallic elements at ultra-trace concentrations. This is especially challenging in sulfuric acid matrices where the presence of sulfur in the acid itself, as well as argon, nitrogen, oxygen, hydrogen and carbon from the plasma gases and surrounding atmosphere, can interfere with the analysis of non-metals by forming polyatomic interferences on the analyte of interest.

The use of an ICP-MS that has a full-length resolving quadrupole before the collision/reaction cell as well as the ability to control the reaction within the cell can dramatically improve detection limits. This allows the detection and quantification of non-metallic elements at low levels.

In this application brief, the ability to detect ultra-trace concentrations of non-metals – boron (B), phosphorus (P), silicon (Si), germanium (Ge), arsenic (As), selenium (Se), bromine (Br) and iodine (I) – in sulfuric acid was demonstrated using a NexION® 5000 Multi-Quadrupole ICP-MS. Here, different cell gases and cell-gas conditions were employed to determine which parameter led to the best limits of detection (DLs) and background equivalent concentrations (BECs) as these are inherently related to the limit of quantification.

PerkinElmer®
For the Better

Experimental

Sample Preparation

Ultrapure water (18.27 MΩ.cm^{-1}) was used to prepare all calibration standards and sample dilutions. Electronic-grade sulfuric acid (98%, Chemitop, Juncheon Gun, Sansusnadan, Korea) was triple-purified using a quartz distillation device and diluted to obtain 9.8% H_2SO_4 for final dilution.

All calibration standards were prepared gravimetrically from either 10 ppm or 1000 ppm single- or multi-element solutions (PerkinElmer Inc., Shelton, Connecticut, USA). In this experiment, hydrogen gas (99.99995%) was generated using a NM-H_2 Plus Hydrogen Generator (PerkinElmer Inc.) to meet the delivery rate and purity requirements of the ICP-MS. Oxygen (99.9999%, UP grade, Daesung Industry, Kyungin-Ro 662, Seoul, Korea) and liquefied ammonia (99.99999%, Semiconductor Grade, TEMC, Chung-Ju, Kukieon Samhang-Gil, Korea) were also used for the analyses.

Instrumentation

In this application brief, the NexION 5000 ICP-MS (PerkinElmer Inc.) was used for all analyses. The ICP-MS conditions specified in Table 1 and analytical conditions specified in Table 2 were applied. In order to remove any trace contamination present in the ICP-MS sample introduction system, deionized water was run through the system for an extended period of time before analysis.

Table 1. NexION 5000 ICP-MS Instrumental Conditions.

Parameter	Value
Nebulizer	PFA-ST3 concentric nebulizer, Probe: 0.25 mm ID
Spray Chamber	SilQ™ cyclonic spray chamber
RF Power	1600 W
Torch and Injector	Demountable quartz torch, SilQ injector 2.0 mm ID
Plasma Gas Flow	15 L.min^{-1}
Scan Types	MS/MS and Mass Shift
Cell Mode	Reaction or Standard
Cell Gas	H_2, O_2 or NH_3

Table 2. Analytes and Analytical Conditions.

Element	Isotope Selection (Q1/Q3)	Cell Mode	Cell Gas
B	11/11	Standard	-
Si	28/28	Reaction	H_2
Si	28/28	Reaction	H_2 +NH_3
P	31/47	Reaction	O_2
P	31/47	Reaction	H_2+O_2
Ge	74/90	Reaction	O_2
Se	78/94	Reaction	O_2
Se	80/96	Reaction	O_2
As	75/91	Reaction	O_2
Br	79/79	Reaction	H_2
I	127/127	Reaction	H_2

* The values set for the analytical conditions are not absolute and may differ slightly depending on the ICP-MS environment.

Mass Shift mode was applied to P, Ge, Se and As, which allowed the removal of polyatomic interferences via exothermic reactions using oxygen to form PO^+, GeO^+, SeO^+ and AsO^+ respectively. Although silicon forms the stable molecular ion SiO^+ in the presence of oxygen gas via an exothermic reaction, N_2^+ and CO^+ have the same mass as silicon and also easily react with oxygen. Thus, interference removal cannot be effectively achieved via a mass-shift reaction with oxygen for this analyte. Consequently, in order to analyze silicon, it is necessary to employ a different means of interference avoidance. When reacted with hydrogen, N_2^+ and CO^+ undergo hydrogenation through a spontaneous exothermic reaction, while silicon only undergoes an endothermic reaction. Due to this difference in reaction speeds, silicon can easily be isolated from N_2^+ and CO^+ by employing a high rejection parameter q (RPq) in the quadrupole Universal Cell. As such, in this experiment, Reaction mode with H_2 was used to remove interferences from N_2^+ and CO^+.

Results and Discussion

As can be seen in Figure 1, the calibration curves of the analytes in 9.8% sulfuric acid all had a correlation coefficient (r^2) of at least 0.9999 with the exception of silicon which had a correlation co-efficient of 0.9998 as determined using the method of standard additions (MSA) for all these analytes.

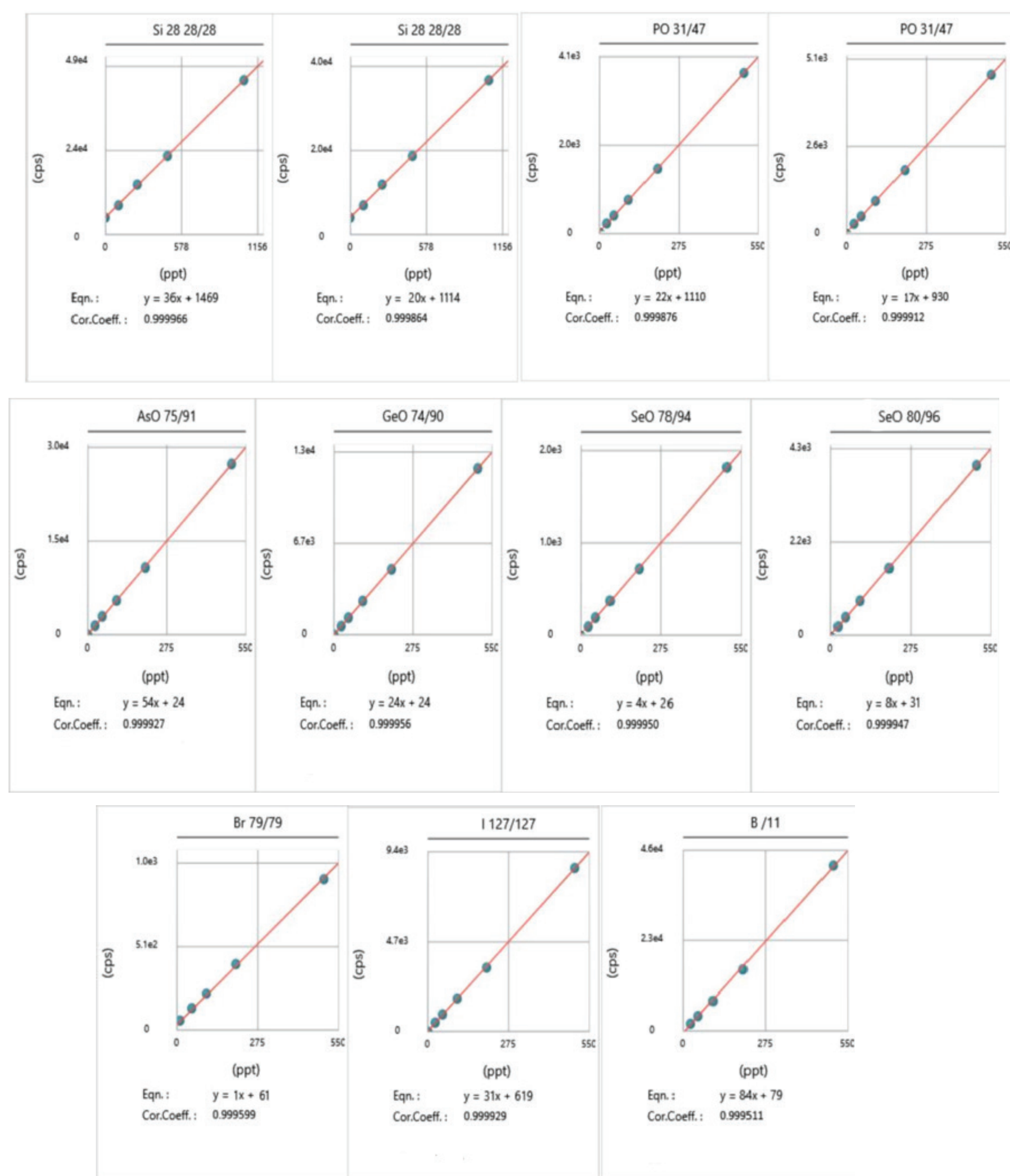

Figure 1. Calibration curves for B, P, Ar, Se, Si, Ge, Br and I in 9.8% sulfuric acid obtained using MSA.

Figure 2 shows the detection limits in 9.8% H_2SO_4 (DLs), where two sets of reaction gases were used for Si and P, and two different isotopes mass-shifted for Se.

In the case of silicon, the analysis took place under two different cell gas conditions, where the first set of conditions involved using hydrogen alone as the reactive gas and the second set used hydrogen with ammonia via on-line gas mixing. Both methods resulted in a DL of *ca.*10 ppt (ng/L). As for phosphorous, the analysis was done using first oxygen alone and second oxygen with hydrogen which were mixed online. For this analyte, the DL was found to be 0.6 ppt with pure oxygen and 0.3 ppt with a mixture of oxygen and hydrogen. The DL was <0.1 ppt for germanium and arsenic, *ca.* 0.5 ppt for selenium and iodine, and *ca.* 2 ppt for bromine. The DL for boron, which was run in Standard mode, was excellent, and with a concentration of *ca.* 0.03 ppt, it is the best-known published DL for this element thus far.

Figure 2. DLs for B, P, As, Se, Si, Ge, Br and I in 9.8% sulfuric acid.

Concentrations of eight non-metals, which are typical contaminants in semiconductor processes, were evaluated in 9.8% (v/v) H_2SO_4 (non-purified and purified) (Figure 3). From this data, it is evident that most of the impurities were effectively removed from the sulfuric acid solution via distillation with the exception of phosphorus, which could not be effectively removed. This is thought to be due to the chemical properties of phosphorus and sulfur and their tendency to form non-volatile compounds. Concentration results from the purified acid can serve as BECs for all analyzed elements.

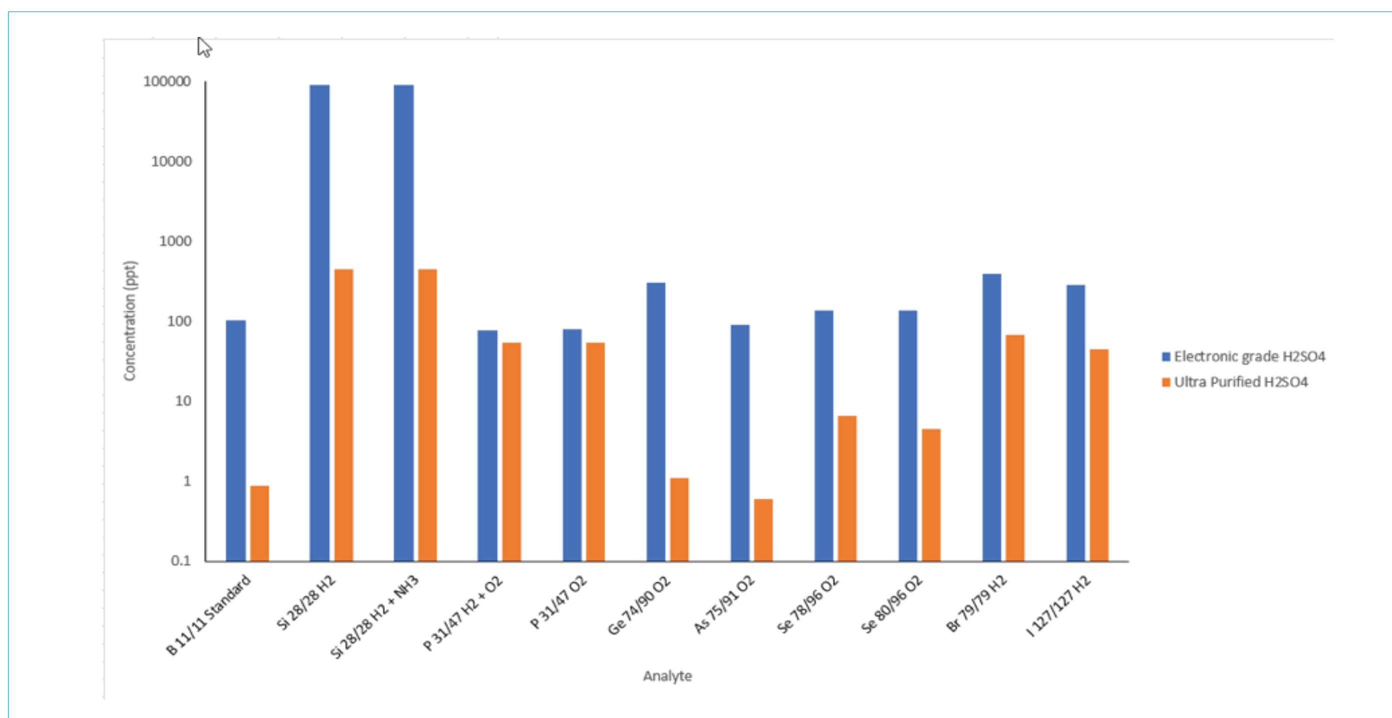

Figure 3. Br, P, Ar, Se, Si, Ge, Br and I content (ppt) in electronic-grade sulfuric acid and purified sulfuric acid.

Conclusions

Being able to achieve ultra-low DLs and BECs for non-metals that are typical contaminants in semiconductor processing is vital in the semiconductor industry sector. This application brief determined the DLs and BECs of typical non-metal contaminants in sulfuric acid solutions using the NexION 5000 ICP-MS.

Excellent limits of detection of 0.1 ppt for B, Ge, and As; 0.5 ppt for P, Se, and I; and 10 ppt for Si and Br were achieved and are a direct consequence of the following proprietary capabilities of the NexION 5000 ICP-MS:

- The quadrupole Universal Cell in combination with the first Transmission Analyzer Quadrupole, which deliver unrivaled interference removal
- The ability to mix gases on the fly, which allows for easy method development
- The patented Triple Cone Interface with OmniRing™ technology which can handle challenging matrices such as 9.8% H_2SO_4

Consumables Used

Component	Part Number
Platinum Sampler Cone	N8145028
Platinum Skimmer Cone	N8161041
Hyper-Skimmer Cone	N8160120
Fixed 2.0 mm Injector UHP Quartz Torch	N8152428
PFA ST3 Nebulizer	N8152378
SilQ Cyclonic Spray Chamber with Matrix Gas Port	N8152539
0.25 mm ST Capillary Line for PFA ST3 Nebulizer	N8122383

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

Copyright ©2021, PerkinElmer, Inc. All rights reserved. PerkinElmer® is a registered trademark of PerkinElmer, Inc. All other trademarks are the property of their respective owners.

170540