Determination of ultra trace elements in semiconductor grade Isopropyl Alcohol (IPA) by high sensitivity ICP-MS

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Key Words

iCAP Q, ICP-MS, IPA, semiconductor, cold plasma, organics

Goal

To determine ultra-trace metal concentrations in semiconductor grade isopropyl alcohol (IPA). Use cold plasma to reduce background equivalent concentrations (BEC) and detection limits (LoD) to demonstrate reproducible ultra trace (ppt) measurements. Demonstrate the reliable switching between hot and cold plasma within a single measurement to maximize sample throughput.

Introduction

Isopropyl alcohol (IPA) is used to solvent clean wafers during production in the semiconductor industry. As IPA comes into direct contact with wafer surfaces, it must be controlled for its trace metal purity. Because of its high elemental sensitivity, ICP-MS is widely used in quality control analyses of materials used in the semiconductor industry. A direct ICP-MS technique for the analysis of IPA would provide a useful control for ultra trace (ppt) levels of analytes in IPA and avoid any contamination caused by sample preparation.

IPA has historically been considered a difficult matrix to analyze directly by ICP-MS due to its high volatility, low viscosity and high carbon content. In this study instead of using kinetic energy discrimination (KED) to remove carbon based interferences from the sample matrix and argon based interferences from the ICP, cold plasma was employed. With this approach the ICP ion source is run at a significantly lower power, effectively suppressing the ionization of argon and carbon and therefore eliminating interfering polyatomic species that would otherwise interfere with target analyte ions. This approach is particularly effective for the alkali metals and permits their direct analysis at the ultra trace concentration levels required by the semiconductor industry.
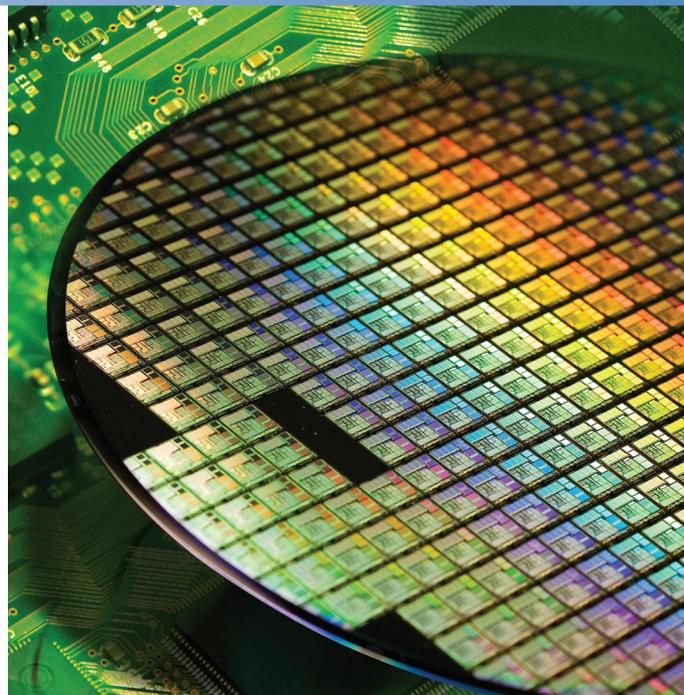
Sample and calibration solution preparation

Precleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultra pure water (18.2 MΩ) and left to dry in a laminar flow clean hood before use. Standards at concentrations of 20, 50, 100 and 200 ppt were prepared by gravimetrically adding the appropriate quantity of a multi-elemental stock solution (prepared from single element standards) directly to the IPA samples. Semiconductor grade IPA was used for the rinse and blank solutions. In order to assess recovery in the IPA matrix, an IPA sample was spiked with 100 ppt and compared with the unspiked sample.

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Instrument configuration

The Thermo Scientific™ iCAP™ Qs ICP-MS was used for all analyses. Due its high transmission interface and proprietary 90 degree ion optics for the removal of neutral species, the iCAP Qs provides the high elemental sensitivity and low backgrounds – in both hot and cold plasma – for the ultra trace determination of trace elements in semiconductor samples.

A dedicated organic matrix sample introduction system was used for the routine, direct analysis of IPA. The introduction system consisted of a 100 µL/min self aspirating PFA micro flow nebulizer (Elemental Scientific, Omaha, NE, USA) and a peltier cooled quartz spray chamber (at -10 °C). Oxygen, precisely regulated by a low flow MFC controlled by the Thermo Scientific™ Qtegra™ software was added to the aerosol stream via a port in the spray chamber elbow to prevent carbon matrix build up on the interface region. A 1.0 mm diameter quartz injector minimized carbon loading of the plasma. Platinum tipped sampler and skimmer cones were necessary because of the oxygen addition.

Operating parameters

The operating parameters used for iCAP Qs ICP-MS used in this work are shown in Table 1.

Table 1. Instrument Parameters

Parameter	Value
Hot plasma power	1350 W
Cold plasma power	800 W
Spray chamber	Quartz cyclonic
Peltier temperature	-10 °C
Hot plasma nebulizer gas flow	0.7 L/min
Cold plasma nebulizer gas flow	1.0 L/min
Oxygen gas flow	50 mL/min
Nebulizer	MicroFlow PFA-100 (self-aspirating)
Injector	1.0 mm I.D., quartz
Interface	Platinum sampler and high sensitivity platinum skimmer
Dwell time	100 ms per peak, 10 sweeps

In this application, the measurement of 26 elements at ultra-trace concentrations in IPA was achieved in less than 5 minutes. This includes sample uptake, analysis and washout as well as the switching time between hot and cold plasma within each measurement.

Result and discussion

The new all-digital, swing frequency RF generator used in the iCAP Qs is lightning fast in comparison to older designs that rely on mechanical matching network to adjust to impedance changes caused by sample matrices and doesn't require a grounded shield to achieve cold plasma. By virtue of this new design, the iCAP Q ICP ion source is significantly more robust so that pure organic solvents can be routinely analyzed at higher sample flow rates than would be possible with older RF generator designs. Running at higher sample flow rates offers improved sensitivity – especially important with semiconductor applications that continually challenge ICP-MS detection limits. The iCAP Q's new RF generator maintains a stable analyte signal over extended measurement periods even when switching between hot and cold plasma in every analysis.

Assigning different analysis modes per isotope is easily performed in the Qtegra software (Figure 1). Low ionization potential (IP) elements (e.g. alkali metals such as Li, Na, Mg, K, Ca as well as first row transition metals such as Cr, Fe etc.) are measured with low backgrounds and high sensitivities in cold plasma and higher IP elements are analyzed in hot plasma. For example, the analysis of magnesium (m/z 24) in IPA under hot plasma conditions is complicated by a carbon dimer species ($^{12}C_2$). As can been seen in Figure 2 and Table 2 however, by using cold plasma the interference at m/z 24 is removed and the sub ppt detection limit (LoD) and background equivalent concentration (BEC) values meet the requirements for ultra-trace analyses in semiconductor relevant materials such as IPA.

Figure 1. Screenshot from Qtegra showing the definition of Hot and Cold plasma per isotope and how to choose the order of the measurement modes used in an analysis.
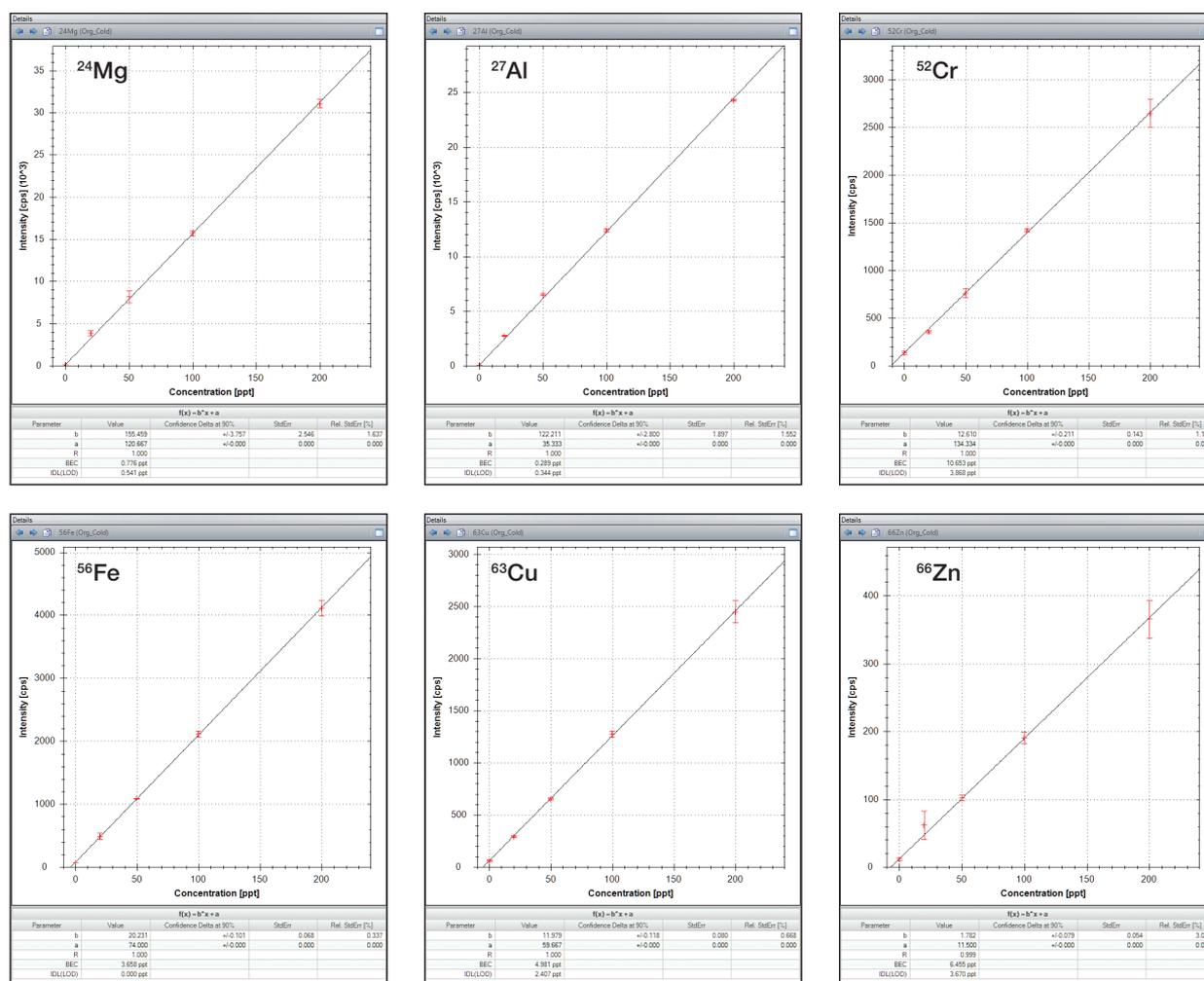
Calibration data

Figure 2. Cold plasma calibration curves with points 20, 50, 100 and 200 (ppt)

Table 2.BEC, LoD and recovery data for the analysis of semiconductor grade IPA. Please note that BEC and LoD values are dependent on the sample measured. Recovery values are shown as the percentage recovery for a 100 ppt spike in IPA. An ^{56}Fe LoD of 0.000 ppt was recorded since all three repeats at ^{56}Fe in the IPA blank gave the same count rate.

	Analysis Mode	BEC (ppt)	LoD (ppt)	Recovery (%)
^{7}Li	Cold	0.031	0.007	99%
^{11}B	Hot	107	29	89%
^{23}Na	Cold	10	0.8	101%
^{24}Mg	Cold	0.78	0.54	101%
^{27}Al	Cold	0.29	0.34	97%
^{39}K	Cold	14	0.31	97%
^{40}Ca	Cold	7.4	3.1	118%
^{51}V	Hot	4.0	1.4	100%
^{52}Cr	Cold	11	3.9	97%
^{55}Mn	Cold	7.3	1.6	97%
^{56}Fe	Cold	3.7	0.000	98%
^{58}Ni	Cold	0.40	0.52	97%
^{59}Co	Cold	1.9	1.2	103%
^{63}Cu	Cold	5.0	2.4	106%
^{66}Zn	Cold	6.5	3.7	109%
^{74}Ge	Hot	5.1	3.9	90%
^{75}As	Hot	7.6	11	107%
^{107}Ag	Cold	0.41	0.42	116%
^{111}Cd	Hot	0.26	0.39	104%
^{115}In	Cold	0.01	0.04	100%
^{120}Sn	Hot	0.10	0.001	103%
^{138}Ba	Hot	0.014	0.014	102%
^{197}Au	Hot	1.0	1.4	86%
^{205}Tl	Cold	0.07	0.22	100%
^{208}Pb	Cold	0.13	0.39	99%
^{209}Bi	Cold	0.001	0.001	98%

Conclusion

The Thermo Scientific iCAP Qs has been shown to offer the high sensitivity and freedom from contamination and interference required for the measurement of ultra-trace (ppt) concentration levels in semiconductor grade IPA. Fast, reliable, in measurement switching between hot and cold plasma even for volatile organic solvents such as IPA is made possible with the new swing frequency RF generator used in the iCAP Q, improving sample throughput.

Products and Reagents used in this Application Note

Organic matrix kit: 1324711
250 mL/min additional gas MFC: 1322530
100 µL/min PFA nebulizer: 1600342
Platinum tipped sample cone: 3601289
Platinum tipped skimmer cone: 1341430

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