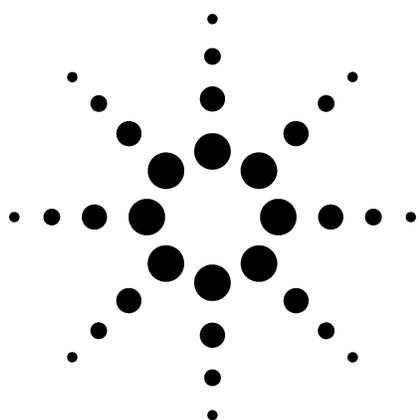


# Direct Analysis of Photoresist and Related Solvents Using the Agilent 7500cs ICP-MS

## Application



## Semiconductor

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### Abstract

**A simple method for analyzing photoresists using reaction cell inductively coupled plasma mass spectrometry is discussed. The Agilent 7500cs ICP-MS, which features a high sensitivity version of the Octopole Reaction System (ORS), was used to analyze photoresist for a full suite of elements. The ORS eliminates all plasma and matrix based polyatomics that interfere with the measurement of elements such as B, Mg, Al, K, Ca, Ti, Cr, Fe, and Zn, which would otherwise limit standard quadrupole ICP-MS operation for this application. Sample preparation is a simple 10× dilution of the photoresist sample (30% resin) in a suitable solvent, followed by direct analysis by the 7500cs.**

### Introduction

Manufacturing integrated circuits (ICs) is a complex process involving numerous steps over a period of weeks. Without constant testing, metal contaminants can be unwittingly introduced at any step of the manufacturing process and particularly during the critical lithography stage. Once a layer

of material, such as an oxide layer, is grown or deposited onto the silicon wafer surface, a light-sensitive liquid-photoresist layer is applied. After it has cured, the photoresist prevents etching or plating of the area it covers. There are several different classifications of resists. In this application note, the analysis of positive resist (p-type), which becomes soluble when exposed to ultraviolet (UV) light, is considered. When processing a wafer with a positive resist, a mask having the required template is aligned between an UV light source and the wafer. UV light shines through the clear portions of the mask thereby exposing the template onto the photo-sensitive resist. The exposed resist becomes soluble to a developer for example, tetra-methyl ammonium hydroxide (TMAH, 2.38%), and is removed from the wafer surface. The “mask pattern” is then etched onto the wafer using either a wet or dry etching process, the remaining undeveloped/hardened photoresist is removed and the process is repeated.

Metal impurities present in the photoresist can cause a distortion of the electrical properties and reliability of the final semiconductor devices, so acceptable limits of impurities are constantly being reduced. Current acceptable levels of metallic impurities in the photoresist (such as Na, Mg, K, Ca, Cr, Mn, Fe, Ni, Cu, and Zn) are in the range 10–30 ppb per element and will become less than 10 ppb soon. Consequently, monitoring these elements in photoresist at ultratrace levels is critical and is routinely carried out by photoresist suppliers and some integrated circuit manufacturers.



A photoresist sample is usually prepared by acid digestion or dry ashing, followed by graphite furnace atomic absorption spectroscopy (GFAAS) analysis. This method is used extensively although it is time-consuming and potentially hazardous. Also, acid digestion or dry-ashing sample preparation can lead to the loss of volatile elements such as boron and arsenic. Other limitations of this approach include the potential introduction of contaminants from the apparatus, acid mixture and other reagents, and the poor sample throughput capabilities of GFAAS. More recently a different approach was developed. Photoresist can be analyzed directly for multiple elements by a combination of simple dilution in an appropriate solvent and analysis using inductively coupled plasma mass spectrometry (ICP-MS). There are a variety of solvents suitable as photoresist diluents, including N-methyl-2-pyrrolidone (NMP), propylene glycol monomethyl ether (PGME) and ethyl lactate. The detection capability of impurities in photoresist is strongly affected by the level of impurities in the solvent. Despite this fact, commercially available ultrahigh purity solvents are difficult to find. This report describes the analysis of photoresist by ICP-MS following a simple dilution in PGME. The solvent was purified in the laboratory prior to the analysis.

## Instrumentation

The Agilent 7500cs ICP-MS instrument is equipped with the Octopole Reaction System (ORS) for the removal of polyatomic species that can interfere with the measurement of some elements as shown in Table 1. A 7500cs fitted with an organic solvent introduction kit (part number G1833-65038) was used in this study. The kit consists of a quartz narrow-bore injector torch (1.5-mm id) with a tapered tip, and spray chamber drain fitting for organic solvents. The Agilent quartz concentric nebulizer (part number G1820-65138) was self aspirated at a sample uptake rate of 68  $\mu\text{L}/\text{min}$ . The specially engineered tapered injector torch, exclusive to Agilent, (part number G1833-65424) is suitable particularly for the analysis of photoresist because the torch requires a narrow injector and is difficult to block. The temperature of the quartz spray chamber was maintained at  $-5\text{ }^\circ\text{C}$ .

## Removal of Carbon

The high carbon content of photoresist, which typically consists of a carrier solvent, photoactive compound, and polymers, can lead to deposition of

carbon on the sampling cone, eventually leading to clogging of the orifice and a reduction in sensitivity. To prevent this, a small amount of oxygen is added into the argon gas line to burn carbon. Oxygen gas is added through a T-connector before the torch. For safety reasons, oxygen should not mix with argon in the spray chamber and it is advisable to use oxygen (20%) diluted with argon. Platinum-tipped interface cones are used instead of nickel cones, which quickly deteriorate, in the much more reactive plasma environment produced by adding oxygen.

## Removal of Spectral Interferences

The photoresist used in this study contains not only carbon, hydrogen, and oxygen but also sulfur as sulfonic acid, giving rise to potential matrix-based polyatomic interferences shown in Table 1. With the introduction of the high-sensitivity 7500cs reaction cell ICP-MS, these spectral background ions can be attenuated using a controlled environment within the ORS cell or by Agilent's cool plasma technology. In this report, data obtained using the 7500cs ORS in helium and hydrogen mode is presented.

**Table 1. Potential Interferences on Preferred Analyte Isotopes**

Analyte	Mass	Polyatomic ions
B	10, 11	$^{12}\text{C}$
Mg	24	$^{12}\text{C}_2$
Al	27	$^{13}\text{C}^{14}\text{N}$ , $^{12}\text{C}^{14}\text{NH}$
K	39	$^{40}\text{ArH}$ , $^{12}\text{C}^{14}\text{N}^{12}\text{CH}$
Ca	40	$^{40}\text{Ar}$
Ti	46,	$^{12}\text{C}^{16}\text{O}_2$
Ti	46, 47, 48	$^{14}\text{N}^{16}\text{O}_2$
Ti	48, 49	$^{32}\text{S}^{16}\text{O}$ , $^{32}\text{S}^{16}\text{OH}$
Cr	52	$^{40}\text{Ar}^{12}\text{C}$
Fe	56	$^{40}\text{Ar}^{16}\text{O}$
Zn	64	$^{32}\text{S}^{16}\text{O}_2$

## Experimental

A simple analytical method was used to analyze the photoresist samples, see Table 2 for the operating parameters used. The optional gas flow rate was set at 0.2 L/min of oxygen (20%) mixed with argon and the torch sampling depth was 8 mm.

Ion lens parameters and ORS gas flow rates were optimized using a blank PGME and a 1-ppb tuning solution containing  $^7\text{Li}$ ,  $^{59}\text{Co}$ ,  $^{89}\text{Y}$ , and  $^{205}\text{Tl}$  in PGME. In non-gas mode, operating conditions were tuned by maximizing the counts for Li, Y, and Tl. In

hydrogen gas mode, the signal response in counts per second (cps) for  $^{59}\text{Co}$  was maximized and the signal response for Ar at mass 40 and ArC at mass 52 were minimized. In helium gas mode,  $^{59}\text{Co}$  was maximized and the background counts at mass 63 and 64 were minimized. The ICP-MS ChemStation software features Multi-tune, which automatically combines different tuning conditions in one analytical run. Results for all elements are presented in a single report.

As photoresist precipitates on contact with water, it is important to ensure there is no water present in the sample introduction system of the ICP-MS. Following ignition of the plasma, when an aqueous solution is used, water is eliminated by introducing a solution of PGME for at least 10 min. Oxygen is added to the plasma gas during this cycle.

**Table 2. 7500cs Operating Conditions**

RF power	1600 W
Sampling depth	8 mm
Carrier gas flow rate	0.6 L/min
Makeup gas flow rate	0 L/min
Optional Gas Flow	20% oxygen in argon
Spray chamber temperature	-5 °C

### Sample Preparation

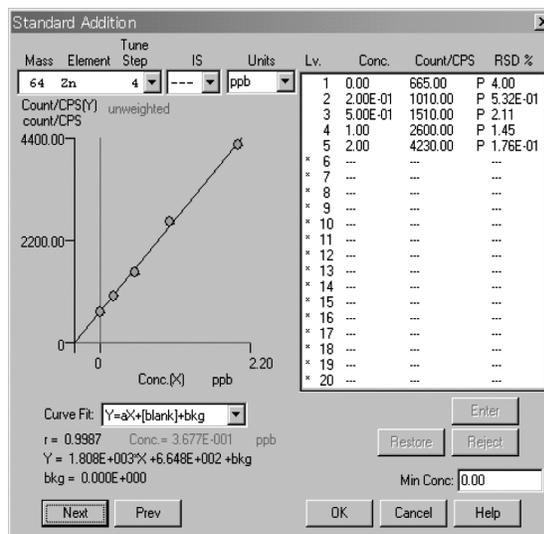
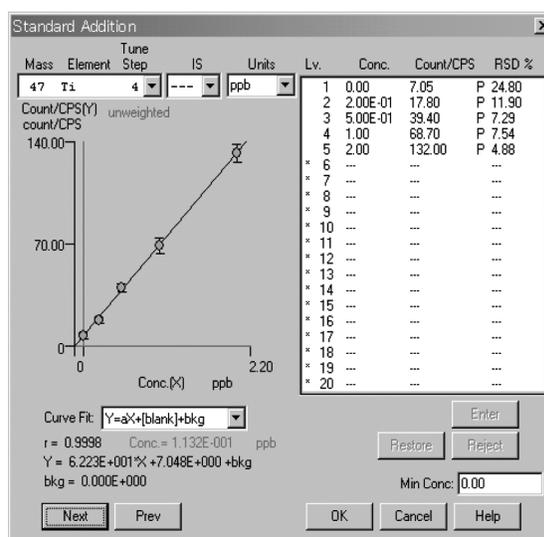
Sample preparation consisted of simply diluting the photoresist samples 1:10 with PGME.

### Method of Quantification

Due to the difference of viscosity between photoresist and PGME, each sample was analyzed separately and the results for PGME were subtracted from the photoresist data to give a net analytical value. Calibrations for each sample were performed using matrix matched PGME and photoresist standards. First, an aliquot of PGME was spiked with a multi-element standard (SPEX) to final concentrations of 0.5, 1.0, and 2.0 ppb. The concentration of the analytes present in the solvent was determined against this external calibration. No internal standards (ISTDs) were added to avoid the risk of contamination. The external calibration avoided the need for time-consuming standard additions, which requires the need to spike every sample. The process was repeated for photoresist. An aliquot of photoresist (diluted to

3% resin in PGME) was spiked to final concentrations of 0, 0.2, 0.5, 1.0, and 2.0 ppb. All other photoresist sample concentrations were determined against this external calibration. Again, no ISTD was used. Concentrations obtained were corrected to account for the dilution factor. Detection limits for each element were obtained from the calibration curves.

The effectiveness of the external, matrix-matched calibration was gauged by spiking the photoresist sample with a multi-element standard at a concentration of 0.5 ppb and calculating recoveries. Figure 1 illustrates representative calibration curves in the matrix matched solution for Ti and Zn. Note the excellent linearity and superb precision that was obtained.



**Figure 1. Photoresist matrix matched calibration curves for  $^{47}\text{Ti}$  and  $^{64}\text{Zn}$ . Helium gas mode was used for both measurements.**

## Data Acquisition

The photoresist sample was allowed to self-aspirate into the ICP-MS using standard 0.3-mm capillary tubing from the Integrated Autosampler (I-AS) – a clean autosampler designed specifically to avoid contamination at the sample introduction stage (product number G3160A). The integration time for each element was 1 s, except for Ti which was 3 s, with three replicate measurements. For the analysis of a suite of 35 elements per sample, the time required was 3.5 min per sample. However, a rinse step using PGME between samples is strongly recommended to prevent signal drift resulting from photoresist precipitation.

## Results

Table 3 shows the detection limits (DL) obtained during this study, for the 1:10 diluted photoresist sample. DLs were calculated using three times the standard deviation ( $n = 7$ ) of the raw counts of the photoresist divided by the slope of the calibration curve. Using the slope of the calibration curve, rather than counts obtained from a standard, takes into account any matrix suppression. The reported DL are fundamentally limited by the metal impurities in the solvent blank (B) that is, in PGME.

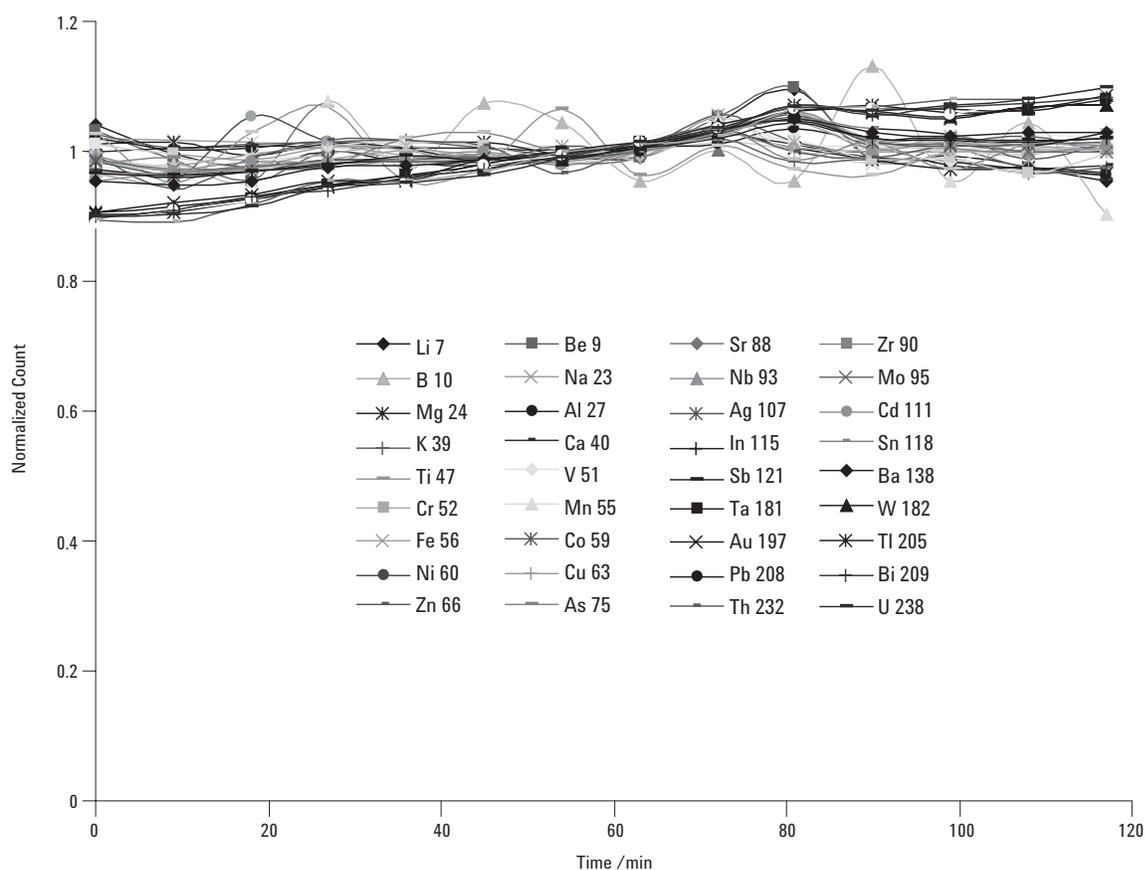
**Table 3. Three Sigma DL in Photoresist and Spike Recovery Data at 0.5-ppb Level for a Full Suite of Elements**

Element (mass)	Plasma power (W)	H <sub>2</sub> Gas flow (mL/min)	He Gas flow (mL/min)	Photoresist DL (ppb)*	Photoresist (A) (ppb)*	PGME (B) (ppb)	A - B (ppb)	Spike recovery (%) 0.5 ppb
Li (7)	1600	–	–	0.01	0.029	0.007	0.022	97
Be (9)	1600	–	–	0.004	0.003	0.003	<0.004	95
B (10)	1600	5	–	0.2	0.279	0.123	<0.2	87
Na (23)	1600	5	–	0.07	2.677	0.027	2.650	82
Mg (24)	1600	5	–	0.03	0.366	0.003	0.364	94
Al (27)	1600	5	–	0.03	0.217	0.019	0.198	93
K (39)	1600	5	–	0.04	1.220	0.059	1.201	93
Ca (40)	1600	5	–	0.02	0.328	0.023	0.269	96
Ti (47)	1600	–	4.5	0.1	0.113	0.008	<0.1	104
V (51)	1600	–	4.5	0.009	0.017	0.004	<0.009	99
Cr (52)	1600	5	–	0.04	0.732	0.001	0.728	97
Mn (55)	1600	5	–	0.004	0.025	0.019	0.024	94
Fe (56)	1600	5	–	0.07	2.317	0.051	2.298	98
Co (59)	1600	–	4.5	0.003	0.020	0.002	0.019	97
Ni (60)	1600	–	4.5	0.06	0.330	0.002	0.281	93
Cu (63)	1600	–	4.5	0.03	0.262	0.001	0.211	97
Zn (68)	1600	–	4.5	0.02	0.369	0.001	0.366	89
As (75)	1600	–	–	0.008	0.010	0.004	0.008	93
Sr (88)	1600	–	–	0.001	0.004	0.040	0.003	91
Zr (90)	1600	–	–	0.007	0.090	0.001	0.089	91
Nb (93)	1600	–	–	0.002	0.010	0.003	0.006	93
Mo (95)	1600	–	–	0.04	0.679	0.005	0.639	96
Ag (107)	1600	–	–	0.001	0.003	0.002	0.002	92
Cd (111)	1600	–	–	0.005	0.008	0.001	0.006	90
Sn (118)	1600	–	–	0.008	0.064	0.001	0.059	89
Sb (121)	1600	–	–	0.003	0.027	0.001	0.025	87
Ba (138)	1600	–	–	0.001	0.007	0.003	0.007	88
Ta (181)	1600	–	–	0.05	0.015	0.002	<0.05	89
W (182)	1600	–	–	0.006	0.032	0.002	0.029	87
Au (197)	1600	–	–	0.003	0.004	0.003	<0.003	86
Tl (205)	1600	–	–	0.001	0.005	0.002	0.003	88
Pb (208)	1600	–	–	0.005	0.019	0.002	0.016	87
Bi (209)	1600	–	–	0.001	0.001	0.003	<0.001	87
Th (232)	1600	–	–	0.0009	0.002	0.001	<0.0009	85
U (238)	1600	–	–	0.0006	0.000	0.001	<0.0006	86

\*Photoresist sample was diluted 1:10 with PGME to give a 3% solution

Table 3 also illustrates 0.5-ppb spike recoveries in 1:10 diluted photoresist for 35 elements. All data was acquired under normal plasma operating conditions that is, 1600W RF forward power. The spike recoveries are good, particularly for difficult elements such as B, Mg, Al, K, Ca, Ti, Cr, Fe, and Zn which suffer matrix and argon based interferences. The results highlight the effectiveness of the ORS for preventing polyatomic ions from reaching the detector.

A 2-hour stability study was performed by adding a 0.5-ppb standard into 1:10 diluted photoresist (3% resin) sample and repeatedly analyzing the spiked sample over a 2-hour period. Instrument stability over this period was excellent with %RSD values typically less than 3% for the majority of elements, despite the complex matrix. A stability plot for all elements is summarized in Figure 2.



**Figure 2. Two-hour stability plot for 35 elements in 3% photoresist sample.**

## Conclusions

Reliable photoresist analysis can be carried out following simple dilution in a suitable solvent so long as the ICP-MS meets several key design considerations:

- The sample introduction system is optimized to handle high sample matrices over extended periods of time. This includes the use of low-flow nebulizers, cooling of the spray chamber and use of a torch injector designed to minimize sample deposition.
- A flexible gas-control mechanism is available to accommodate the need for oxygen addition when analyzing organic solvents.
- There is an effective reaction cell for elimination of polyatomic interferences while maintaining sufficient sensitivity for trace level analysis.

The Agilent 7500cs ICP-MS with ORS meets all of the design criteria outlined above. The results outlined in this application note demonstrate that:

- The optimized sample-introduction system in the 7500cs effectively breaks down the heavy-resist matrix (sample analyzed as 3% resins).
- The ORS eliminates matrix-based interferences on B, Mg, Al, Ti, Cr, and Zn, as well as Ar-based interferences on K, Ca, and Fe.

The combination of these two powerful features provides reproducible measurements of the key analytes at the levels required by the industry.

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