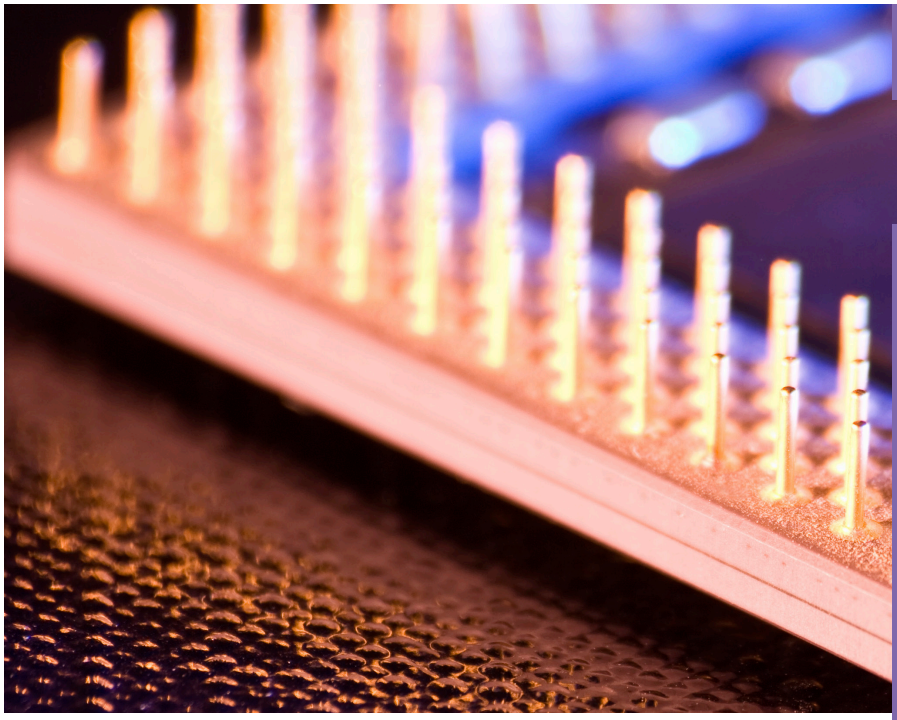

APPLICATION NOTE

Atomic Absorption

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The Determination of Various Elements at Ultra-trace Levels in Ultrapure Acids and Photoresist Stripper Solutions by Graphite Furnace Atomic Absorption

Introduction

Analytical techniques capable of ultra-trace metal determination in the sub-ppb range are required in the semiconductor industry for the analysis of very complex sample matrices and corrosive acids. To meet these requirements, high-performance techniques such as inductively coupled plasma mass spectrometry (ICP-MS) are preferred for rapid multi-element analysis. However, there are cases wherein process/facilities troubleshooting involves only a few elements, typically environmental elements, such as the alkaline elements sodium (Na), calcium (Ca), and aluminum (Al) or transition elements iron (Fe) and copper (Cu), need to be easily and rapidly determined. In these cases, graphite furnace atomic absorption spectrometry (GFAAS) would be extremely useful.

Graphite furnace AAS is a highly specific and selective technique in which complex sample matrices can be removed by the optimized temperature programs. The interferents in the sample matrix are removed and separated from the analyte, resulting in almost interference-free analysis, which leads to accurate results. The graphite furnace also acts as a site for pre-concentration for the elements which is particularly important for ultra-trace determination in samples such as organic photoresists and highly concentrated corrosive acids.

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Experimental

Instrumentation and Reagents

A PerkinElmer PinAAcle™ 900Z atomic absorption (AA) spectrometer was used for all measurements. The PinAAcle 900Z AA spectrometer is equipped with a transversely heated graphite atomizer (THGA) and an AS 900 autosampler. Samples were automatically pipetted into the THGA tubes using an AS 900 autosampler. Coded cableless Lumina™ single-element hollow cathode lamps (HCLs) were used as the light source under the operating conditions as recommended by the manufacturer. To avoid contamination from the lab environment, the autosampler and graphite furnace compartment were covered. All flasks and polyethylene cups required for preparation of the blank solutions and standards were pre-soaked in 5% (v/v) nitric acid for 24 hours prior to filling with ultra-pure water for storage before use. The autosampler's polyethylene rinse bottle was freshly filled with ultra-pure water every day prior to analysis. UltraClean THGA graphite tubes with integrated platforms were used for all measurements.

The PinAAcle 900's TubeView™ furnace camera (Figure 1) is extremely useful, allowing the user to adjust the pipette tip to the most appropriate depth in the graphite tube and also monitor any residue buildup on the platform during the analysis. The camera is also used during method development of the temperature program to verify the drying steps, ensuring that sample boiling or spattering does not occur. In the case of organic samples such as photoresist stripper solutions with surfactants and TMAH, the TubeView camera is a handy tool to determine the optimized drying temperature and holding time for complete dryness prior to the pyrolysis step.

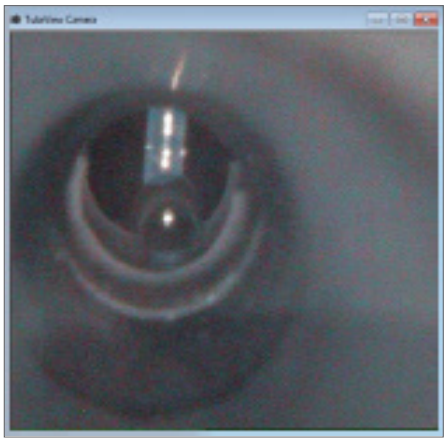

Figure 1. AS 900 autosampler depositing a droplet of water in the THGA tube as seen using the TubeView furnace camera.

Twenty microliters of standard or sample solutions, as well as the 5 µL spike recovery standard, were dispensed with the autosampler.

Since the sample matrix of these reagents can be removed from the furnace with proper optimization of drying and pyrolysis, the addition of a chemical modifier was not required with exception of Al, where 5 µL of 0.015 mg $Mg(NO_3)_2$ was used as the matrix modifier. Three replicate readings were taken for each analyte.

The Method Development feature of the software automated the optimization of the temperature program for each element in a specific matrix. In addition, the aim of this study was to find a single optimized temperature program for each individual element suitable for use in as many chemicals as possible. Through the aid of the Method Development software and the TubeView camera, an additional drying step is included mainly to achieve complete dryness of photoresist developer. The instrument settings and temperature for each element are tabulated in Tables 1 and 2.

Table 1. Instrument settings used on the PinAAcle 900Z AAS.

Element	Wavelength (nm)	Slit (nm)	Lamp Type	Lamp Current (mA)	BOC Time (sec)	Read Time (sec)
Na	589.0	0.2	HCL	4	2.0	4.0
Ca	422.7	0.7	HCL	10	2.0	6.0
Cu	324.7	0.7	HCL	15	2.0	4.0
Fe	248.3	0.2	HCL	30	2.0	4.0
Al	309.3	0.7	HCL	25	2.0	3.0

Note: Read delay was 0 seconds for all elements.

Table 2. Temperature/time programs for the determination of Al, Ca, Cu, Fe, and Na in various semiconductor application chemicals.

	Temp (°C)	Ramp Time (sec)	Hold Time (sec)	Internal Flow (mL/min)
Al 309.3 nm				
Dry Step 1	110	5	25	250
Dry Step 2	150	15	40	250
Dry Step 3	200	5	10	250
Pre-treatment	1400	10	20	250
Atomization	2300	0	3	0
Clean out	2500	1	5	250
Ca 422.7 nm				
Dry Step 1	110	5	25	250
Dry Step 2	150	15	50	250
Dry Step 3	200	5	10	250
Pre-treatment	1100	15	25	250
Atomization	2500	0	6	0
Clean out	2550	1	3	250
Cu 324.7 nm				
Dry Step 1	110	5	25	250
Dry Step 2	150	15	40	250
Dry Step 3	200	5	10	250
Pre-treatment	1200	10	25	250
Atomization	2000	0	4	0
Clean out	2450	1	3	250
Fe 248.3 nm				
Dry Step 1	110	5	25	250
Dry Step 2	150	15	40	250
Dry Step 3	200	5	10	250
Pre-treatment	1350	10	25	250
Atomization	2100	0	4	0
Clean out	2500	1	5	250
Na 589 nm				
Dry Step 1	110	5	25	250
Dry Step 2	150	15	40	250
Dry Step 3	200	5	10	250
Pre-treatment	900	20	30	250
Atomization	1600	0	4	0
Clean out	2500	1	5	250

Results

Calibration Statistics

All elements were calibrated with 3 µg/L and 6 µg/L standards and showed calibration correlation coefficients (R^2) better than or equal to 0.999, as shown in Figure 2. The sensitivities (as characteristic mass) were all within 20% of the "cookbook" values[1].

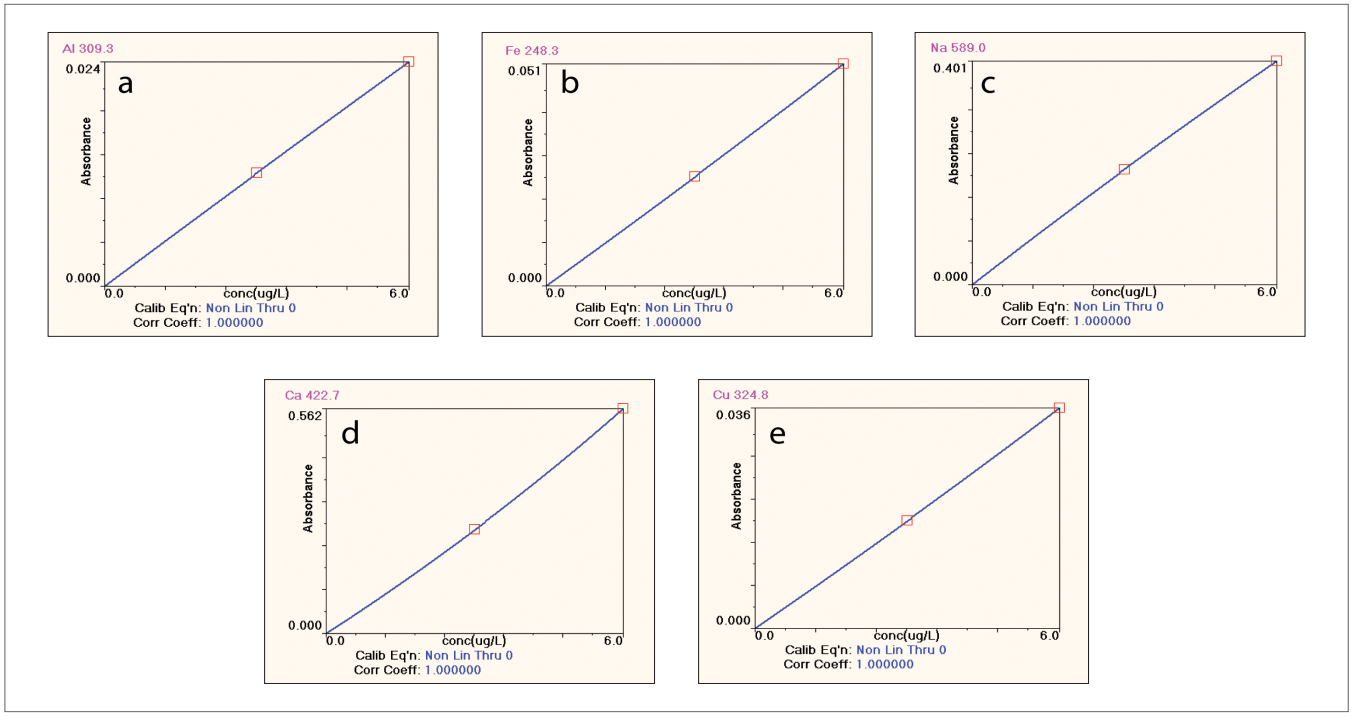

Figure 2. Calibration curves for (a) Al, (b) Fe, (c) Na, (d) Ca, and (e) Cu.

Quality Control

Quality control (QC) and recovery checks were analyzed to determine accuracy of the method. In this case, only specific elements per customer requirement were tested for each chemical. The recovery data for this study are tabulated in Table 3 below.

Table 3. The spike recovery results in the determination of Al, Ca, Cu, Fe, and Na in various semiconductor application chemicals.

	Unspiked Sample (µg/L)	Spiked Result (µg/L)	Spike Conc. (µg/L)	Recoveries (%)
Al				
NH_4OH (29%)	< MDL	1.09	0.9	121
Metal Etch	0.18	1.06	0.9	98
Thinner	1.08	1.90	0.9	91
Stripper 2	0.26	1.12	0.9	96
Ca				
NH_4OH (29%)	0.34	1.21	0.9	97
TMAH diluted	0.09	1.03	0.9	104
Metal Etch	0.17	0.99	0.9	91
PGMEA	0.003	0.82	0.9	91
Thinner	0.11	0.95	0.9	93
H_2O_2	0.28	1.13	0.9	94
Cu				
NH_4OH (29%)	0.08	1.03	0.9	106
TMAH diluted	< MDL	0.96	0.9	107
Metal Etch	0.04	0.86	0.9	91
PGMEA	0.003	0.978	0.9	108
Thinner	< MDL	1.01	0.9	112
H_2O_2	0.15	0.98	0.9	92
Stripper 2	0.05	1.03	0.9	109
IPA	< MDL	0.87	0.9	97
Stripper 1	0.058	0.89	0.9	92
SC2	0.018	0.82	0.9	89

	Unspiked Sample (µg/L)	Spiked Result (µg/L)	Spike Conc. (µg/L)	Recoveries (%)
Fe				
NH_4OH (29%)	< MDL	1.03	0.9	114
TMAH diluted	< MDL	0.96	0.9	107
Metal Etch	0.64	1.56	0.9	102
PGMEA	0.08	1.03	0.9	106
Thinner	0.10	1.07	0.9	108
H_2O_2	< MDL	0.96	0.9	107
Stripper 2	0.75	1.70	0.9	106
H_3PO_4 ,20x diluted	1.10	3.24	2	107
Na				
NH_4OH (29%)	< MDL	0.88	0.9	98
TMAH diluted	0.05	0.87	0.9	91
Metal Etch	0.38	1.23	0.9	94
PGMEA	0.01	0.88	0.9	97
Thinner	0.04	0.99	0.9	106
H_2O_2	< MDL	0.79	0.9	89

Table 4. IDLs and MDLs for Al, Ca, Cu, Fe, and Na.

	IDL	MDL					
Elements	Blank (µg/L)	H_2O_2 (µg/L)	NH_4OH (µg/L)	NMP (µg/L)	IPA (µg/L)	TMAH (µg/L)	Average (µg/L)
Al	0.02	0.9	0.9	1.2	1.5	0.6	1.02
Ca	0.04	0.15	0.07	0.16	0.045	0.03	0.091
Cu	0.01	0.06	0.06	0.07	0.06	0.09	0.068
Fe	0.02	1.2	0.9	0.02	0.6	0.6	0.664
Na	0.005	0.06	0.015	0.15	0.15	0.015	0.078

The SEMI guideline for process chemical purity requires the analytical data to achieve a spike recovery between 75 and 125%. The data show that the furnace programs are robust for different chemical matrices and achieve the recovery criteria stipulated by the SEMI C1-0310 Guide for the Analysis of Liquid Chemicals[2].

The instrument detection limits (IDLs) were calculated by taking ten replicates of a blank and taking three times the standard deviation. The method detection limit (MDL) was calculated by taking seven replicates of a clean, unspiked sample (low concentration level) and taking three times the standard deviation. The SEMI C10-1109 Guide for Determination of Method Detection Limits[3] requires the MDL to be determined from the average of multiple MDL determinations taken over at least two days. In this work, however, since our aim is to build a common method for various chemical types, the MDLs are the average of MDLs obtained with individual chemicals. Five chemicals were chosen for this work based on the difference in their matrix and physical properties, and the detection limits are tabulated in Table 4.

The goal of this work was to emulate the operation of a real laboratory, so the calibration standards were chosen accordingly. However, because the lowest standard (3 µg/L) is much greater than the MDL, the MDLs are artificially elevated. Achieving lower MDLs requires using a lower standard, closer to the true MDLs.

Conclusion

The method developed on the PinAAcle 900Z AA spectrometer has proven to be successful in analyzing the elements of importance in different matrices, increasing productivity for the quality control of important chemicals used in the manufacturing facilities. Good recoveries were achieved, with MDLs meeting the SEMI C1-0310 requirement.

The same methods can also be used on PerkinElmer's PinAAcle 900T, which has the same patented transversely-heated longitudinal Zeeman background correction graphite furnace. These temperature programs may also be applicable on the Massman-type furnace (as in the PinAAcle 900H) with some modification.

Built-in features of the PinAAcle 900 series, such as the TubeView furnace camera and Method Development in the software, are extremely useful to aid in method development for the optimized temperature programs for the analytes. The Syngistix™ for AA software on the PinAAcle 900 series makes it fast and easy to get from sample to results. By reducing the time required for method development, sample analysis and report generation, Syngistix streamlines every step of your workflow for enhanced laboratory productivity. The software completely automates furnace method development, allowing for optimized pyrolysis and atomization temperatures as well as sample and modifier volumes. It also allows method creation, review or reprocess data offline, and even adding samples anytime without interrupting the active analysis. The intuitive Syngistix for AA software is an additional tool that is also important in the routine operation of the instrument. It has the standard QA/QC statistical tool that helps in the routine daily monitoring of the quality of the chemicals used in the manufacturing facilities.

References

1. *"Analytical Methods for Atomic Spectrometry"*, PerkinElmer Corporation, 1999.
2. SEMI C1-0310 Guide for the Analysis of Liquid Chemicals.
3. SEMI C10-1109 Guide for Determination of Method Detection Limits.

Consumables Used

Component	Part Number
2.0 mL Polyethylene GFAA Autosampler Cups	B0087056
UltraClean THGA Graphite Tubes with Integrated Platform	B3140362
$Mg(NO_3)_2$ Matrix Modifier	B0190634
Lumina Al Hollow Cathode Lamp	N3050103
Lumina Ca Hollow Cathode Lamp	N3050114
Lumina Cu Hollow Cathode Lamp	N3050121
Lumina Fe Hollow Cathode Lamp	N3050126
Lumina Na Hollow Cathode Lamp	N3050148

Component	Part Number
Pure-Grade Al Standard (1000 mg/L)	N9300184 (125 mL) N9300100 (500 mL)
Pure-Grade Ca Standard (1000 mg/L)	N9303763 (125 mL) N9300108 (500 mL)
Pure-Grade Cu Standard (1000 mg/L)	N9300183 (125 mL) N9300114 (500 mL)
Pure-Grade Fe Standard (1000 mg/L)	N9303771 (125 mL) N9300126 (500 mL)
Pure-Grade Na Standard (1000 mg/L)	N9303785 (125 mL) N9300152 (500 mL)

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