

CONTAMINATION CONTROL: REMOTE SAMPLING

On-Line Remote Sampling into an ICP Mass Spectrometer to Monitor Trace Metal Contamination Levels in Semiconductor Process Chemical Baths

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IT IS RECOGNIZED THAT THE PERFORMANCE OF integrated circuits (IC) is adversely affected by trace metal contamination levels of the high-purity chemicals used in the semiconductor manufacturing process. Traditionally, metallic impurities have been measured by sampling the chemical bath and analyzing it off-line, typically using techniques such as inductively-coupled plasma mass spectrometry (ICP-MS), which has been validated by SEMI in its Book of Semiconductor Standards (BOSS) [1]. Unfortunately, if a contamination problem is suspected, it can be some time before the result is known and the problem corrected. Attempts have been made to develop on-line monitoring systems by either locating the measuring technique close to the source of the sample or by pumping the liquid sample through extended lengths of plastic tubing to the spectrometer. Unfortunately, the majority of these methods fell short of expectations, mainly because of contamination problems, element loss from absorption by the tube walls and the time delay when pumping liquids such long distances. An additional problem created by transporting liquid samples is that this method is not ideally suited to applications where the sample volume is limited.

However, the increasing demand to reduce analysis times and lower overall production costs has led researchers to take a fresh look at this area. One such investigation that is in its early stages of development is an automated on-line sampling project undertaken as a venture between PerkinElmer Life and Analytical Sciences of Shelton, Connecticut, Elemental Scientific Inc. of Omaha, Nebraska, IAS Inc. of Tokyo, Japan and Micron Technology Inc. of Boise, Idaho. These four companies have collaborated in a feasibility study into on-line sampling of semiconductor chemical baths by using a Remote

Aerosol Transfer System to transport a sample aerosol to an ICP-MS system situated in a remote laboratory, where the trace element contamination levels are automatically measured.

TRADITIONAL SAMPLING OF PROCESS CHEMICAL BATHS

The main limitation with traditional methods of analyzing semiconductor chemical baths is that typically, a laboratory person has to put on a clean suit, collect the sample, bring it back the lab, carry out some kind of sample preparation and eventually analyze it. Clearly, the elapsed time between knowing there is a problem and understanding what the problem is could be very costly, both in terms of manufacturing down time and degradation of product quality. One way of alleviating these bottlenecks is to utilize on-line monitoring of impurity levels in the chemical baths within a manufacturing plant. The major benefit of this approach is that trace element contamination levels in chemical baths can be continuously monitored on a real-time basis, which not only enhances productivity, improves quality and increases device yields, but also enables the operators to identify potential contamination problems far earlier than traditional methods of sample collection. Early research into on-line monitoring techniques used measuring equipment situated in the same location as the chemical baths. Unfortunately, many of the corrosive chemicals used in the manufacturing process created a very hostile environment for the instruments, which clearly impacted analytical cleanliness and sample contamination. Another approach was to pump the sample liquid at flow rates of approximately 1 mL per minute to the ICP mass spectrometer for analysis. These approaches had limited success for reasons mentioned earlier,

but additionally they had the reputation of being difficult to use, had reliability problems and were generally not easy to automate because of the need to use both cool and normal plasma conditions to determine the full suite of semiconductor elements [2].

ON-LINE SAMPLING METHODS

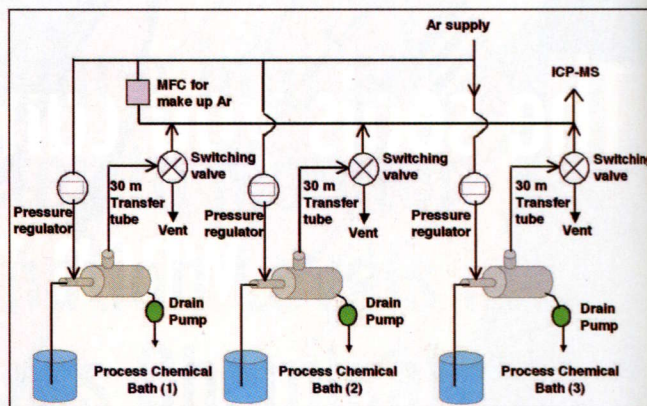
A novel way of getting around these kinds of problems is to create an aerosol just after the sample is taken and then transport the aerosol to a laboratory-based ICP-MS for analysis. This refinement to the traditional kinds of on-line monitoring techniques takes a liquid sample from the process chemical bath, creates a fine-particle aerosol with a nebulizer, and transports the resulting aerosol via narrow-bore tubing to an ICP mass spectrometer in a laboratory clean-room, located some distance from the manufacturing plant. This not only eliminates the problems associated with pumping liquids but is also a far more practical solution to housing a sophisticated, ultra-sensitive ICP-MS next to the chemical baths. However, to adopt this sampling method for a real-world semiconductor manufacturing environment, it is important to know the limitations of transporting an aerosol such long distances from the location where the sample was taken. For that reason, the main focus of the feasibility study was to better understand elemental adsorption by the walls of the transfer tube by determining analytical figures of merit such as sensitivity loss, rinse-out times, signal stability and calibration characteristics.

REMOTE-SAMPLING FEASIBILITY STUDY

Based on input from the four companies, it was decided to set up a laboratory-based experiment where three semiconductor cleaning chemicals were sampled, nebulized and transported to the remote ICP-MS system for analysis. In this set-up, the sample solutions were self-aspirated by argon flow into a nebulizer and spray chamber placed close to each of the sample containers. The generated aerosol was then transported to the ICP-MS through a 30 m (97.5 feet) x 8 mm (0.3 inches) I.D. perfluoroalkoxy (PFA) transfer tube using the argon gas flow. The sample flow was switched from one sample to another by a PFA switching valve located near the ICP-MS, which enabled even limited amounts of sample to be transported very quickly, therefore minimizing the sample uptake time. A schematic of the set-up is shown in Figure 1.

The ICP-MS system used in this experiment was an ELAN DRC II supplied by PerkinElmer Sciex, based in Concord, Ontario, Canada. The Remote Aerosol Transfer System components like spray chambers, nebulizers, sampling devices, switching valves and transfer lines were designed, supplied and customized by Elemental Scientific and IAS. The benefits of using ion-molecule chemistry in a dynamic reaction cell (DRC) for the analysis of semiconductor chemicals are well-documented in the literature [3, 4, 5, 6]. The ability to reduce many polyatomic interferences and determine the most critical elements made it ideally suited to handle the demands of this

FIGURE 1



Experimental set-up of remotely sampling three semiconductor process chemicals into an ICP-MS system positioned 100 feet away.

TABLE 1

Parameter/System	Setting/Type
Nebulizer & Spray Chamber	PFA concentric type and PFA Scott type/Quartz cyclonic, APEX desolvating system
Torch Injector	Pt
Sampling/Skimmer Cones	Pt
RF Power	1550 W
Plasma Gas Flow	18 L/min
Aux. Gas Flow	1.8 L/min
Nebulizer Gas Flow	1.0 - 1.1 L/min
Cell Gas for DRC	NH ₃
Integration Time	1 sec/mass

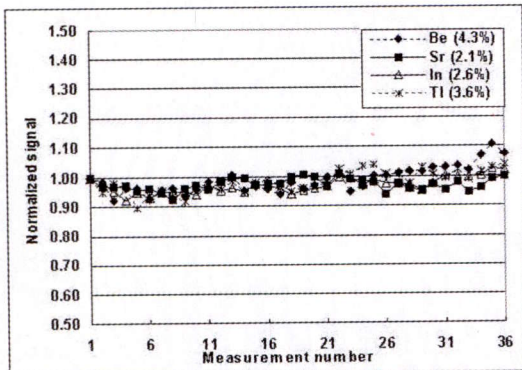
Operating conditions for the ELAN DRC II ICP-MS used in this remote sampling study.

type of automated remote-sampling application. For elements that do not require the DRC mode, the instrument can be run in the standard mode where no reactive gases are used in the cell. The system has the added advantage of using one set of hot plasma conditions, so there is no compromise in ionization conditions and as a result, complex semiconductor chemicals can be analyzed against simple aqueous/nitric acid calibration standards [7]. The instrument operating conditions are listed in Table 1.

ANALYTICAL FIGURES OF MERIT

For this investigation, three types of common semiconductor cleaning solutions were prepared by diluting high purity-grade chemicals provided by Tama Chemicals Inc. of Tokyo,

FIGURE 2



The complete 46 hours of the stability run for the four internal standard (IS) elements in Sample 3 (exact run times for each sample are shown in Table 2).

Japan. The chemicals and final concentration used in the experiment were as follows:

SAMPLE 1: 1 % HF

SAMPLE 2: 2.5 % NH₄OH + 3.5 % H₂O₂

SAMPLE 3: 3.5 % HCl + 3.5 % H₂O₂

It was felt that there were four major questions that needed to be addressed in order to make an evaluation as to whether this approach was going to work in a semiconductor production environment. These questions were:

- Is it possible to transfer an aerosol sample up to 100 feet (without being pumped) and achieve good multielement recovery and long-term stability?
- Can good calibration curves be achieved at low analyte concentrations for both DRC and standard condition elements?
- By transporting a solution aerosol such long distances, is there a significant change in analyte concentration over time due to absorption into the walls of the transfer tubing?
- How long does it take to stabilize the instrument when switching valves from one sample to another?

Let's take a closer look at how these critical questions were answered.

EVALUATION OF LONG-TERM STABILITY USING SELF-ASPIRATION

Because self-aspiration was being used to transport the samples, there was a concern that a difference in sample viscosities would affect the nebulization efficiency and therefore the uptake rate of each chemical being analyzed. The classic way to compensate for these types of sample transport effects in ICP-MS is to use internal standardization (IS), where a non-analyte element of similar mass and ionization potential is

TABLE 2

QC Standard	Time (hr:min)	0	13:30	23:50	30:30	%RSD (%)
Be		4152	4082	3989	3949	1.9
Sr		70351	67993	65616	64748	1.8
In		52701	47190	48468	47831	2.2
Tl		30634	27578	28278	28170	2.4
Sample 1	Time (hr:min)	0	5:45	12:15	15:00	RSD (%)
Be		3525	3586	3701	3664	1.4
Sr		64764	63449	63649	62698	1.4
In		47136	43923	44566	44457	2.0
Tl		28714	26137	26769	26488	2.7
Sample 2	Time (hr:min)	0	5:45	12:15	16:30	RSD (%)
Be		2112	2164	2262	2333	4.3
Sr		55663	55306	57177	56700	3.8
In		38576	37787	39992	39475	2.7
Tl		24075	23327	24976	24191	3.1
Sample 3	Time (hr:min)	0	5:45	12:15	45:50	RSD (%)
Be		2788	2590	2747	2952	3.0
Sr		45786	43525	45276	44232	2.2
In		31353	29607	30340	31712	2.4
Tl		20636	19417	19010	20633	3.0

The intensity in counts per second (cps) of the IS elements in all four samples at selected periods. Note: strontium (in red) was determined in DRC mode, while the others (in blue) were determined in standard mode.

added to all the samples and standards. The signals for the internal standards are then monitored and a compensation made to the concentration of the analytes based on the variation in the internal standard signals. Changes in the intensity of the internal standard signal over time are a good indication of the instrument's long-term stability.

For this application, the following internal standard elements/masses were used: 5 mg/L ⁹Be, and 1 mg/L ⁸⁸Sr, ¹¹⁵In and ²⁰⁵Tl. To make this stability experiment as realistic as possible, a blank of 1 percent HNO₃ and a standard of 1 mg/L (ppb) of 25 elements in 1 percent HNO₃ (plus the internal standard elements) was used to establish one set of calibration curves for all samples. The following samples were then repeatedly analyzed by the ELAN DRC II coupled to an AS 93 autosampler from PerkinElmer Life and Analytical Sciences in the order shown below, over a time period of 15 to 46 hours.

- 1) Sample 1 (1% HF) + IS
- 2) Followed by Sample 1 + 100 ng/L (ppt) spike +IS
- 3) Followed by Sample 2 (2.5 % NH₄OH/3.5 % H₂O₂) + IS
- 4) Followed by Sample 2 + 100 ng/L (ppt) spike + IS
- 5) Followed by Sample 3 (3.5 % HCl/3.5 % H₂O₂) + IS
- 6) Followed by Sample 3 + 100 ng/L (ppt) spike + IS
- 7) Back to Sample 1 and so on ...

All analyte and internal standard intensities were monitored over this 15- to 46-hour time period. The system was re-calibrated and a QC sample of 500 ng/L (ppt) in 1 percent HNO₃ was analyzed every 30 samples. The intensity in counts per second (cps) of the IS elements in all four samples at selected times in the stability run, together with their percentage of RSD, are shown in Table 2. The complete 46-hour long-term stability run of the four internal standard elements in Sample 3 is shown graphically in Figure 2.

The spike recovery data calculated from the unspiked samples and 100 ng/L (ppt) spiked samples were in the range of 90 to 110 percent, while precision (percentage RSD) over the 15 to 46 hours was less than 1 percent for most of the analyte elements. Percentage of RSD for all 25 analytes at 100 ng/L (ppt) (except for the QC sample, which was 500 ppt) can be seen in Table 3.

LOW-LEVEL CALIBRATION CURVES FOR DRC AND NON-DRC ELEMENTS

The internal standard data shown in Table 2 shows that their intensities are approximately 20 percent of what would be anticipated with a standard sample introduction system because of the 30 meters of transfer line. However, detection limits calculated by dividing the standard deviation of the blank solution by the sensitivity were not severely compromised and were on the order of 10 ng/L (ppt) and below for all 25 elements. Because the sensitivity was low compared to conventional nebulization, it was important to evaluate the capability of the remote sampling method to carry out low-level quantitation of both DRC-based and standard condition elements. For this test, 0, 2, 5, 10 and 50 ng/L (ppt) multielement standards in 1 percent HNO₃ were used to evaluate its calibration characteristics. The samples were nebulized with a PFA concentric nebulizer and transported to the ICP-MS through the 30-meter transfer tubing, which was connected directly to the base of the torch of the ICP-MS system. One set of calibration standards was then run sequentially to check the capability of the system to analyze ultra-trace levels. Six of the calibration curves (before internal standardization) are shown in Figure 3. As can be seen, very good linearity was obtained for both DRC and standard condition elements, even at ultra-trace levels.

ELEMENTAL ABSORPTION INTO TRANSFER TUBING WALLS

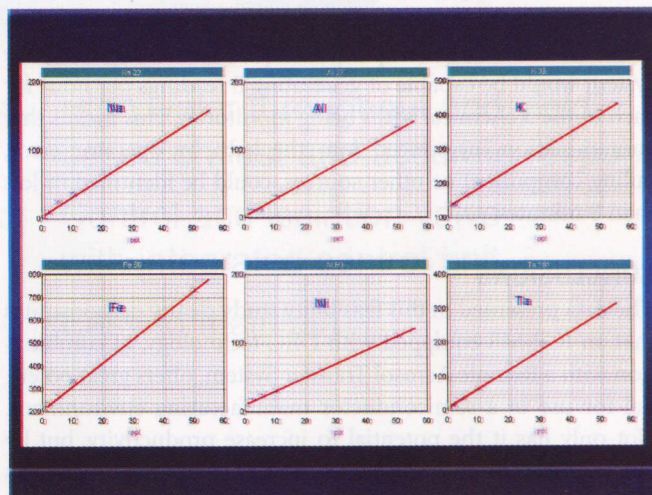
It had been observed with previous sampling designs, which transported liquids (as opposed to an aerosol) over long distances, that some elements suffered a dramatic loss in sensitivity over time from absorption into the tubing walls. It was therefore important to evaluate the elemental absorption characteristic of the Remote Aerosol Transfer System. Using the same conditions that generated the low-level calibration curve data, a 13-hour long-term stability test was performed with a 1 mg/L (ppb) multi-element (39 analytes) standard solution to evaluate whether there was any significant absorption of

TABLE 3

Ele.	QC STD	Sample 1	Sample 2	Sample 3
Li	1.13	0.41	0.65	0.58
B	2.20	0.71	0.79	1.04
Na	0.94	0.26	0.47	0.27
Mg	0.90	0.47	0.71	0.42
Al	0.80	0.38	1.02	0.36
K	0.72	0.26	0.33	1.10
Ca	0.68	0.20	0.28	0.33
Ti	0.87	0.70	1.56	0.70
V	0.79	0.25	0.37	0.32
Cr	0.72	0.55	3.86	3.22
Mn	3.16	0.29	0.32	1.36
Fe	1.17	0.52	0.51	1.78
Co	0.72	0.30	0.32	0.32
Ni	0.70	0.21	0.33	0.81
Cu	0.52	0.21	0.93	0.32
Zn	0.70	0.30	0.91	0.34
Ge	1.04	0.34	0.46	0.46
As	2.11	0.64	1.00	1.19
Mo	0.93	0.26	0.38	0.45
Cd	0.66	0.25	0.32	0.40
Sn	0.68	0.16	0.25	1.46
Sb	0.67	0.18	0.25	0.38
Ba	0.49	0.20	0.18	0.24
W	0.64	0.24	0.27	0.23
Pb	0.67	0.17	0.23	1.00

Percentage of RSD for all 25 analytes at 100 ng/L (ppt) and QC sample, at 500 ng/L (ppt). Note: DRC elements are shown in red, while standard condition elements are shown in blue.

FIGURE 3



Calibration Curves for 0, 2, 5, 10, and 50 ppt potassium, iron and aluminum (using DRC conditions) and sodium, nickel and tantalum (using standard conditions) without the use of internal standardization.

the analytes by the transfer tubing. The results of some key elements are shown in Figure 4. It can be clearly seen that excellent stability was obtained, with signal RSDs in the order of 1 to 2 percent for most of the elements.

SIGNAL STABILIZATION TIMES

A critical evaluation criterion is the time taken for the sample aerosol to make its way to the spectrometer, reach a steady-state signal (before the instrument takes intensity readings) and be fully washed out before the next sample measurement cycle begins. This becomes even more complex when three or more sample streams are being monitored. For this reason, the measurement cycle time, together with the time taken to switch sampling valves, will have a direct impact on the number of samples the system can analyze in a given time. To better understand signal stabilization and switching times, three internal standard elements were spiked into the nitric acid blank, and Samples 1 and 2 as follows:

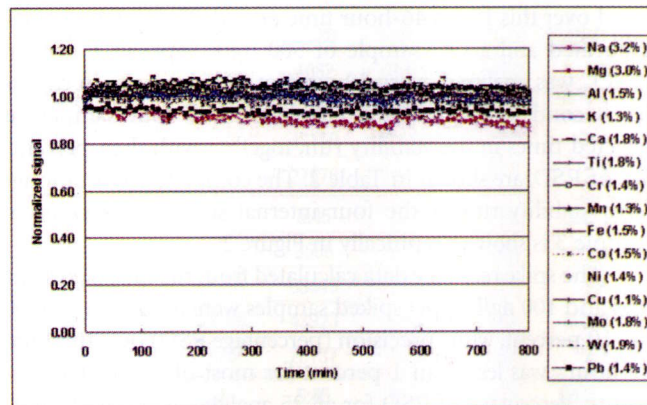
- 1 mg/L (ppb) ^{103}Rh in a HNO_3 blank
- 10 mg/L (ppb) ^{89}Y in Sample 1
- 1 mg/L (ppb) ^{115}In in Sample 2

Using the remote sampling device shown in Figure 1, transient signals were monitored to check the effect of switching on signal stabilization. Each sample was transported 30 meters. The valve was switched every 100 seconds, and the three samples were introduced into the ICP-MS alternately. The results of this test are shown in Figure 5. As can be seen, the signals were stable after 20 seconds of switching the valve, and three orders of magnitude signal reduction could be achieved in 50 seconds, when the valve is switched to another sample. Therefore, if we use a real-world scenario of an integration time of 0.5 second for the determination of 30 elements, the analysis time will be less than 30 seconds per replicate. If we add 1 minute to switch from DRC to standard cell conditions and 1 minute to washout the sample, this translates into analyzing a sample every 2.5 minutes or 24 measurements per hour. So, for example, with the remote sampling set-up shown in Figure 1, the system would be capable of generating 8 readings per hour for each of the 3 chemical baths being monitored. This means that contamination introduced into the bath by operator error, failing component or other sources, could be identified in less than 8 minutes.

CONCLUSIONS

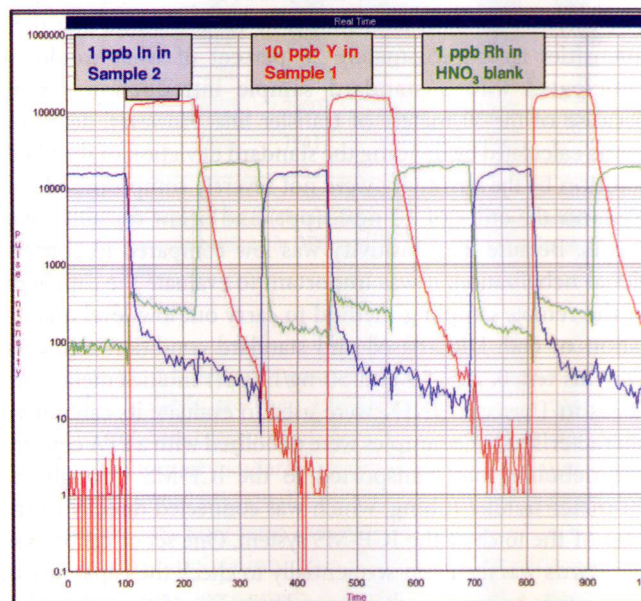
The data presented in this feasibility study clearly demonstrates that an ICP-MS equipped with DRC technology, in combination with a Remote Aerosol Transfer System, offers great potential for use in a semiconductor manufacturing environment. Not only has it the potential to increase productivity, but by continuously monitoring trace element contamination levels on a real-time basis, it enables problems or possible catastrophes in the fab to be averted before they impact manufacturing downtime or product quality. However, it is important to emphasize that this has been a laboratory study. The next phase

FIGURE 4



Thirteen-hour stability run for a selected group of analytes nebulized through 30 m of transfer tubing.

FIGURE 5



Stabilization times of sample switching with the remote sampling system.

undertaken by these four companies takes it into a manufacturing environment. Only when it generates the same kind of data in a fab can it be considered a truly successful venture. ☎

REFERENCES

1. *Book of Semiconductor Standards (BOSS)*, Semiconductor Equipment and Materials International (SEMI), San Jose, California, 2005.
2. K. Sakata and K. Kawabata, *Spectrochimica Acta*, 49B, 1027, 1994.
3. D. S. Bollinger and A. J. Schleisman, *Atomic Spectroscopy*, 20, 2, 60-63, 1999.
4. K. Kawabata, Y. Kishi and R. Thomas, *Spectroscopy*, 18 (1), 2-9, 2003.
5. C. M. Ping, K. Kawabata, Y. Kishi and R. Thomas, *Micro*, April, 2003.
6. K. Kawabata, Y. Kishi and R. Thomas, *Analytical Chemistry*, October, 2003.
7. J. M. Collard, K. Kawabata, Y. Kishi and R. Thomas, *Micro*, January, 2002.