MICROELECTRONICS

PPQ ANALYSIS OF HIGH-PURITY DI WATER USED IN SEMICONDUCTOR FABS

H igh-purity water is the most commonly used solvent in the semiconductor fabrication process. Historically, the technology for the purification of high-purity water has been adequate to maintain the purity levels needed for the semiconductor industry. While minor changes over the past decade have been made, the basic technology involved in the purification process has basically remained the same. Even analytical technologies have been inadequate to measure the true metallic impurity levels in semiconductor-grade high-purity water. However, decreases in line-width geometries of semiconductors have lead to new concerns about impurities in high-purity water.

Committees for the International Technology Roadmap for Semiconductors (ITRS) set specifications for materials based on these future semiconductor device geometry trends (1). The ITRS committee that sets specifications for semiconductor water purity has determined that specifications must be changed to meet the requirements of the new line-width geometries of the next generation of semiconductors. Proposed metallic impurities guidelines from 2005 through 2013 are detailed in Table A. Current high-purity water purity specifications for semiconductor fabs require no metallic impurity should be greater than 1 part-per-trillion (ppt) for the following critical metals: alu-

*By David Bollinger
and Hugh Gotts, Ph.D.*
Air Liquide-Balazs Analytical Services

minum (Al), arsenic (As), barium (Ba), calcium (Ca), cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), tin (Sn), titanium (Ti), and zinc (Zn). The ITRS committee has agreed that these requirements will be adequate throughout the year 2007. However, these specifications change for 2008 and beyond to 0.5 ppt., or 500 parts-per-quadrillion (ppq).

Analytical methodologies have been developed for the analysis of high-purity water to current ITRS specifications (2-4). However, the new 2008 guidelines represent a new challenge for the analytical field because they will call for the detection of impurities below the capability of most analytical methods. New analytical methods are needed to not only detect whether the new specifications can be met, but also provide a quantitative determination of metallic impurities for a system to determine whether the system truly meets the new specifications.

Experimental

The preparation of new sampling bottles required two steps: PFA sample bottles were leached with a mixture of 10% HNO_3 [Fisher Optima grade] / 10% HF [Stella SA-X grade, Japan] for two weeks, followed by soaking in 10% HF for two weeks. Prior to sample acquisition, each sample bottle was rinsed with 5% HF [Stella SA-XX grade, Japan] followed by copious amounts of semiconductor grade high-purity water.

High-purity water samples were collected by allowing high-purity water from selected sampling points to flow directly into the specially cleaned sample bottles. Wafer fab high-purity water bath samples for fab troubleshooting purposes were collected using the persfluoroalkoxy (PFA) sampler shown in Figure 1. Following sample collection,

the high-purity water samples were acidified with a semiconductor-grade acid and allowed to stand for at least 4 hours. Aliquots of the collected sample were then transferred to pre-cleaned PFA evaporation bottles. The bottles were weighed and evaporated to dryness using an ultra-clean sample evaporation system. The patented, custom-design evaporation system is constructed with all PFA parts and features a non-contact heat source (Figure 2) (5). Residues were dissolved in a solution of 2% HNO_3/2% H_2O_2 (semiconductor grade) for final analysis.

Existing methods for the determination of metallic impurities to current ITRS specifications required a pre-concentration to bring the analyte concentration in the solution into the dynamic range of the analysis instrument. A constant total pre-concentration factor was used for all samples for further investigations. Elemental analyses were carried out on a PE-Sciex 6100 DRC 2 Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometer (DRC ICP-MS) (PE-Sciex, Norwalk, Conn.) equipped with a quartz spray chamber (PE-Sciex, Norwalk, Conn.), and 50 microliters per minute (µL/min) PFA micronebulizer

Figure 1. High-purity water PFA Sampler. The sampler uses no O-rings or moving parts allowing for ultra-clean sample collection.
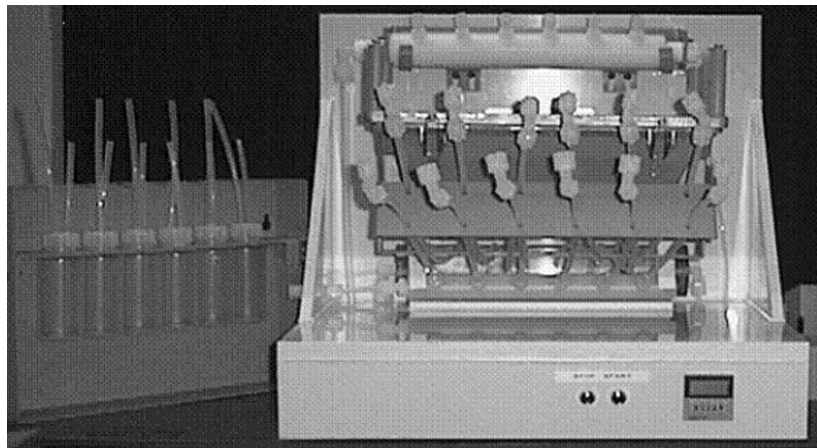
Figure 2. Sample evaporation system. This patented system uses only ultra-high-purity PFA parts, contains no O-rings, and utilizes a non-contact heat source that evaporates and pre-concentrates chemical samples.

(Elemental Scientific, Omaha, Neb.). The dynamic reaction cell uses post-plasma ion-molecule reactions to eliminate atomic and molecular isobaric interferences that are created within the plasma during analysis. The DRC ICP-MS instrument design has been described in detail by Tanner, Baranov, and Vollkopf (6). Individual working standards were prepared by serial dilution from separate NIST-traceable spectroscopy standards (High Purity Standards, Charleston, S.C.). Semiconductor-grade 18.2 MΩ deionized water was used throughout the experiments for dilutions.

Discussion

PPQ sampling contamination considerations. While it is impossible to eliminate all potential contamination sources, one can take steps to minimize contamination effects. However, what can be seen is that virtually anything that comes in contact with the sample, whether solid, liquid, or gas, has the potential to influence the final analysis results. Over several years, analysis of many materials has been done to identify the highest purity materials possible for use in such difficult sample collection efforts.

As a rule of thumb, sampling is generally revered as routine, with only modest training needed to complete the task adequately. However, sampling at the ppq levels requires more detailed examination. One example of contamination potential is the sampling environment itself. Sampling in uncontrolled environments can lead to particulate matter dissolved into the sample by either falling into open sampling bottles, or by Venturi effects seen in the airflow around the high-purity water-sampling stream. Static charge also plays a large part in contamination because particulates are especially attracted to the high-purity bottles made from copolymer materials that are prone to static buildup. One particle of iron oxide, for example, about 0.1 micron (μm) in size dissolved in 1 milliliter (mL) of water is equivalent to 2 femtogram per gram (fg/g) (7). Because of this contamination risk, routine sampling collection procedures are inadequate for testing to ppq levels.

Another point of consideration once the sample has been collected is how the sample will be transported to the analysis location. Factors such a heat, pressure, light, surface-to-volume ratio, physical agitation, packaging material, and container positioning will all affect the final result. One must take steps to minimize contamination from these factors. Some of these factors can be minimized by shipping the sample bottles to and from the sampling site double bagged. The packaging material Vermiculite is never used due to the significant levels of contamination from the fine dust that makes up this material. Foam packing is generally used to keep samples from shifting. One also must consider if the person who transports the sample is knowledgeable about these factors. Samples can be compromised simply because the person shipping the samples was not aware such precautions were needed.

Additionally, contamination may be introduced even during the analysis process. During sample transfer steps for example, the bottles for the sampling and analysis can be contaminated if precautions are not taken. Even in an environment, such as a Class 10 cleanroom, the possibility of contamination cannot be ruled out. Assuming an airflow of 90 linear feet per minute, 10 calcium oxide (CaO) particles per cubic foot (ft^3) that are 0.5 μm in size could still be present in the air. If one transfers a 50 mL sample into a vessel with a 1½-inch opening for about 2 minutes to conduct sample transfer, 2 particles could enter the vessel, yielding a possible contamination of 6 fg/g (7). The threat of contamination is still present even in this type of cleanroom environment. Therefore, every step in the sample analysis train, from sample collection to sample analysis and data interpretation has been keenly looked at and potential sources of contamination minimized.

Solving Problems in the Fab

The methods developed for measurement of high-purity water at current ITRS specification levels have been used to solve process problems in real fabs. With the use of these methods, problem areas inside fab processing units were identified. Two such examples are listed below.

Case #1. Two different high-purity water distribution systems were investigated for stainless steel contamination. Many components (pumps, and UV sterilizers) are typically constructed with stainless steel parts that can lead to contamination in the high-purity water stream. Samples were collected from two different semiconductor fab areas. Additionally, the two different high-purity water distribution systems were sampled at several points (Table B). This sampling strategy allowed for the accurate characterization of several wafer fab sites. High-purity water point-of-use (POU) samples were also taken using the PFA sampling device. This device makes use of all PFA material with no moving parts or O-rings. Simply compressing and releasing the sample bottle creates a vacuum that allows the transfer of sample into the pre-

cleaned sample bottle. The only point of contact for the sample is PFA tubing and PFA sampling bottles. Two POU high-purity water samples from distinct sources were compared (Table C). The data clearly demonstrate differences in the high-purity water. These differences helped identify contamination sources at the POU, and throughout the distribution system.

Case #2. Hot and cold high-purity water supply systems leading to a wafer rinse bath tool were investigated for ppq-level impurities. Total reflection X-ray fluorescence (TXRF) analysis of process wafers done previously indicated a Cu source somewhere within the rinsing procedure. Further investigations into the source of the Cu contamination lead to the possibility that one of the high-purity water supplies could be suspect. However, analysis of the high-purity water baths showed Cu results below the detection limit of routine analytical procedures. Three samples were collected from the system, one from the cold supply and two from the hot supply. ppq analysis results of the different samples collected are shown in Table D. Results clearly indicate a Cu contamination

source coming from the first hot rinse supply. These results enabled the fab to locate a defective part within the high-purity water stream coming from the first high-purity water rinse supply.

2008 ITRS Specifications
The work mentioned above demonstrates the ability our laboratories have to collect and analyze high-purity water samples to current ITRS specifications. However, the question now becomes whether or not these methods could be further expanded to analyze impurities in high-purity water to such an aggressive specification as to what is called for in 2008 and beyond. To answer this question, experiments were performed by pre-concentration of 8 different high-purity water samples collected from our own high-purity water system. The samples were spiked at the new 2008 specification level of 0.5 ppt (500 ppq) for each ITRS-required element. A pre-concentration factor of 60 was used for these experiments because the desired spike levels were a factor of two lower than previous validation work.

The new detection limits calculated for this work indicated the spike levels would be significantly above detection

levels. The DRC gas parameters used to eliminate isobaric interferences, and resulting calculated method detection limits are shown in Table E. Acceptable spike recoveries, from 84% to 115%, were observed for all elements tested (Table F). The data not only reflects the ability to detect impurities at the 2008 specifications, but also reflects the ability to reliably quantitate these impurities at such levels. These methods could allow a fab to completely determine if they are within compliance of the new ITRS specifications.

The ITRS committee is also currently considering expanding the critical metals list from the current 18 elements to a 30-element list currently used for analysis of other chemicals used in the semiconductor industry. Work has been done to test if this expanded list is feasible to meet. As seen in Table G, the extended list of metals is possible. Au, Pd, and Ru are elements also included in the proposed extended metals list. The feasibility studies for these elements will be tested in future experimental trials.

Conclusion
Analysis at the ppq level requires careful examination of the data to identify

TABLE C
ppq Analysis Results of Two Different POU Sources

Element	POU I (ppt)	POU II (ppt)
Ca	<0.85	<0.85
	<0.85	<0.85
Ti	<0.15	1.31
	<0.15	1.19
Cr	1.07	1.25
	1.04	1.15
Fe	0.74	<0.50
	1.66	<0.50
Ni	8.49	0.73
	8.14	0.47
Cu	2.68	2.69
	2.46	2.62
Zn	<1.00	2.08
	<1.00	2.10

TABLE D
ppq Analysis of Hot and Cold High-Purity Water Supplies for Cu

Sample	Cu
Rinse bath, cold DI H_2O supply	<0.17
	<0.17
First rinse bath hot DI H_2O supply	4.74
	4.92
Second rinse bath hot DI H_2O supply	<0.17
	<0.17

TABLE E
DRC Gas Parameters and New Calculated Detection Limits

Element	Interfering Species	Method Detection Limit (ppt) (3 sigma)
^7Li	--	0.11
^{23}Na	--	0.11
^{24}Mg	$^{12}C - ^{12}C^+$	0.15
^{27}Al	$^{11}B-^{16}O^+$, $^{12}C-^{14}N^+$, $^{28}Si^+$	0.17
^{39}K	$^{38}Ar-^1H^+$	0.24
^{40}Ca	$^{40}Ar^+$	0.18
^{48}Ti	$^{36}Ar-^{12}C^+$, $^{14}N-^{16}O-^{18}O^+$	0.09
^{52}Cr	$^{40}Ar-^{12}C^+$, $^{38}Ar-^{14}N^+$	0.14
^{55}Mn	$^{40}Ar-^{15}N^+$, $^{40}Ar-^{14}N-^1H^+$	0.04
^{56}Fe	$^{40}Ar-^{16}O^+$, $^{41}Ar-^{14}N-^1H^+$	0.05
^{59}Co	$^{40}Ar-^{19}F^+$, $^{40}Ar-^{18}O-^1H^+$	0.13
^{58}Ni	$^{40}Ar-^{18}O^+$, $^{40}Ar-^{17}O-1H^+$	0.12
^{63}Cu	$^{31}P-^{18}O-^{16}O^+$	0.13
^{64}Zn	$^{36}Ar-^{28}Si^+$, $^{128}Xe^{2+}$	
^{75}As	$^{40}Ar-^{35}Cl^+$, $^{40}Ar-^{19}F-^{16}O^+$	0.13
^{120}Sn	--	0.12
^{138}Ba	--	0.08
^{208}Pb	--	0.11

*For 2008 ITRS specifications.

sources of contamination in both the sampling and analysis procedures. The methods described here have shown that detection and quantification at ppq levels are possible for the analysis of ultra clean high-purity water systems. We have demonstrated, with the use of our PFA sampling system, the ability to obtain clean samples from process baths. Ultra-clean sampling, sample pre-concentration, and DRC-ICP-MS analysis allow the ability to characterize and diagnose problem areas in high-purity water process streams at the ppq level.

Meeting the requirements for the new specifications of high-purity water purity beginning in 2008 will be challenging. Analysis of high-purity water samples to determine whether or not a system can meet these new specifications also represents special challenges. However, it has been shown that these analytical challenges can be met if the proper precautions in sampling and analysis are taken with regards to minimizing contamination sources. Data reveal the possibility of contamination can be significant in any step of the analysis process. Minute particles from the sampling environment, conditions present during sample transport, sampling containers, and even analytical environment and materials all can affect the final result. Investigations into the effects of these factors, and minimizing their contamination contributions, have lead to success in the analysis at the ppq levels.❏

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TABLE F
0.5 ppt (500 ppq) Spike Recoveries*

Element	Method Blanks Blk #1	Blk #2	Avg.	0.5 ppt Method Spikes #1	#2	#3	#4	#5	#6	#7	#8	Average % Recovery	Coefficient of Variation
Li	0.01	0.02	0.02	0.49	0.55	0.56	0.53	0.60	0.56	0.50	0.55	106%	7.0%
Na	0.45	0.41	0.43	0.95	1.01	0.99	0.90	0.95	0.99	0.99	0.94	107%	4.0%
Mg	0.04	0.04	0.04	0.69	0.54	0.61	0.66	0.55	0.63	0.62	0.59	114%	8.0%
Al	0.03	0.04	0.04	0.67	0.57	0.61	0.67	0.53	0.59	0.68	0.56	115%	9.0%
K	0.02	0.09	0.06	0.51	0.49	0.55	0.71	0.56	0.51	0.57	0.67	103%	14.0%
Ca	0.12	0.11	0.12	0.64	0.61	0.64	0.60	0.60	0.66	0.78	0.70	108%	9.0%
Ti	0.20	0.02	0.11	0.51	0.51	0.54	0.56	0.54	0.48	0.52	0.57	84%	6.0%
Cr	0.02	0.01	0.02	0.47	0.50	0.44	0.55	0.52	0.43	0.56	0.52	97%	10.0%
Mn	0.00	0.01	0.01	0.56	0.55	0.56	0.53	0.55	0.53	0.53	0.55	108%	2.0%
Fe	0.04	0.01	0.03	0.53	0.54	0.55	0.56	0.48	0.48	0.51	0.50	106%	3.0%
Co	0.00	0.01	0.01	0.61	0.54	0.55	0.56	0.48	0.48	0.51	0.50	105%	8.0%
Ni	0.06	-0.01	0.03	0.53	0.49	0.56	0.58	0.49	0.58	0.59	0.58	105%	8.0%
Cu	-0.01	-0.01	-0.01	0.51	0.53	0.50	0.55	0.56	0.50	0.52	0.42	104%	8.0%
Zn	0.03	0.01	0.02	0.52	0.55	0.63	0.56	0.63	0.49	0.56	0.61	110%	9.0%
As	0.05	0.03	0.04	0.50	0.42	0.46	0.49	0.46	0.53	0.40	0.46	85%	9.0%
Sn	0.02	0.00	0.01	0.53	0.45	0.53	0.54	0.53	0.45	0.53	0.55	101%	8.0%
Ba	0.01	0.01	0.01	0.53	0.52	0.54	0.56	0.55	0.47	0.53	0.53	104%	5.0%
Pb	0.02	0.01	0.02	0.51	0.55	0.54	0.55	0.47	0.58	0.58	0.54	104%	7.0%

*For the proposed ITRS 2008 metals list. The data was collected using 8 separate high-purity water samples.

TABLE G
0.5 ppt (500 ppq) Spike Recoveries and Calculated Method Detection Limits*

Element	Method Blanks Blk #1	Blk #2	Avg.	0.5 ppt Method Spikes #1	#2	#3	#4	#5	#6	#7	#8	Average % Recovery	Coefficient (3-sigma) Variation
Be	0.08	0.03	0.06	0.51	0.51	0.59	0.62	0.50	0.59	0.55	0.47	98%	0.16
V	0.02	0.02	0.02	0.46	0.51	0.49	0.52	0.50	0.37	0.43	0.47	90%	0.15
Ga	0.00	0.00	0.00	0.49	0.49	0.52	0.53	0.51	0.41	0.49	0.52	99%	0.11
Ge	0.00	0.00	0.00	0.45	0.52	0.51	0.51	0.50	0.47	0.50	0.48	99%	0.07
Sr	0.00	0.00	0.00	0.51	0.51	0.51	0.52	0.50	0.50	0.52	0.51	102%	0.02
Zr	0.00	0.00	0.00	0.50	0.53	0.49	0.54	0.49	0.51	0.52	0.52	103%	0.05
Nb	0.00	0.00	0.00	0.47	0.51	0.50	0.52	0.50	0.48	0.49	0.49	99%	0.05
Mo	0.00	0.00	0.00	0.51	0.54	0.54	0.56	0.50	0.53	0.50	0.55	106%	0.07
Ag	0.01	0.01	0.01	0.54	0.40	0.46	0.51	0.55	0.49	0.48	0.42	95%	0.17
Cd	0.00	0.00	0.00	0.49	0.47	0.50	0.47	0.54	0.57	0.52	0.55	103%	0.11
In	0.00	0.00	0.00	0.48	0.48	0.48	0.50	0.50	0.49	0.49	0.50	98%	0.03
Sb	0.00	0.00	0.00	0.47	0.48	0.50	0.57	0.59	0.50	0.56	0.51	105%	0.18
La	0.00	0.99	0.99	0.50	0.49	0.50	0.52	0.52	0.48	0.49	0.45	99%	0.07
Ta	0.00	0.00	0.00	0.45	0.41	0.49	0.52	0.50	0.40	0.48	0.49	94%	0.13
W	0.00	0.00	0.00	0.51	0.49	0.51	0.51	0.55	0.33	0.56	0.54	100%	0.22
Pt	0.00	0.00	0.00	0.51	0.57	0.57	0.58	0.53	0.47	0.43	0.44	103%	0.18
Ti	0.00	0.00	0.00	0.46	0.51	0.50	0.51	0.54	0.51	0.46	0.47	99%	0.09
Bi	0.00	0.00	0	0.49	0.49	0.52	0.49	0.52	0.45	0.52	0.53	100%	0.08

*For the proposed ITRS 2008 extended metals list.

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Author David Bollinger is a research chemist at Air Liquide-Balazs Analytical Services located in Dallas, Texas. He holds a B.S. degree in biochemistry from the University of North Texas, and has worked as a research chemist in the semiconductor area for more than 15 years. He has authored and co-authored numerous papers and presentations on semiconductor process chemical analyses and contamination studies.

Coauthor Hugh Gotts, Ph.D., is the director of research and development for Air Liquide-Balazs Analytical Services and is responsible for the development of analytical methods for lab based as well as on-line analyses. He has worked for Philips Semiconductors developing the measurement of online thin-film analysis and established Analytical Services Group, LLC., which provided consulting and analysis services to major Silicon Valley companies. Dr. Gotts has a Ph.D. in physical chemistry from UC Santa Cruz.