ICP – Mass Spectrometry

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Ultratrace Interference-Free Analysis of Solar-Grade Silicon Wafers by ELAN DRC II ICP-MS

Abstract

A new, simple sample-preparation method which results in minimal contamination has been developed for the ultratrace interference-free analysis of solar-grade silicon wafers using an ELAN® DRC II ICP-MS. Using Dynamic Reaction Cell™ (DRC™) technology with patented dynamic bandpass tuning (DBT) and robust hot-plasma conditions, the determination of many critical elements, including boron and phosphorus at the ppt (ng/L) level, without impact from interfering species, is shown.

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Introduction

With the increased interest in renewable energy, there are growing opportunities for solar photovoltaic (PV) systems. According to market research, PV is expected to account for over 50% of the world's total electricity generated by renewable-energy sources by 2070. It is reported that today approximately 90% of the worldwide solar photovoltaic installations use mono- or multi-crystalline silicon wafers in the solar cells. Silicon wafers represent half or more of the cost of silicon solar cells. Reducing the cost to produce silicon wafers is one of the key challenges facing the industry, and using low-cost solar-grade silicon is a common approach. This often results in silicon with higher levels of impurities, in the 4N-6N range (99.99 - 99.9999% pure), which can significantly affect wafer yields and solar-cell performance. Shortly after the 1983 introduction of the first ELAN Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), the solar-cell industry recognized the many possibilities of this new technology. Not only could detection limits be lowered for several elements beyond any other technology, but the determination of several elements at the sub-ppbw (parts per billion by weight) level in a single sample could also be achieved with confidence.[1,2]

While ICP-MS is known to be one of the most sensitive techniques for trace-elemental analysis, it is extremely important to address the significant solvent-related and silicon-based polyatomic interferences that are generated, as well as the matrix suppression effects due to the bulk silicon content of the solutions. These issues arise when directly analyzing solutions with a dissolved silicon matrix. Among the impurities in silicon wafers, boron and phosphorus are of particular importance as they function as dopants and must be below threshold levels. In addition, they must be in a specific balance for proper solar-cell performance. However, boron and phosphorus are classically difficult elements to be accurately determined by ICP-MS. More importantly, common sample-preparation procedures for the analysis of boron in solar-grade silicon wafers often involved the addition of another more-aggressive acid, such as sulfuric acid, to remove the bulk silicon completely using a high-temperature evaporation process. Some procedures also recommend the addition of mannitol to retain boron in solution while heating.[3] Unfortunately, these two actions pose a higher risk of sample contamination and increased interferences, potentially degrading method detection limits (MDLs). Since current ICP-MS instrumentation is relatively unaffected by the sample matrix, the sample preparation has become of paramount importance to achieving the lower detection limits and faster speed of analysis requested by the solar-cell industry. Direct analysis is more attractive because it does not contaminate the sample and generally does not require bulk-silicon removal via time-consuming hot-plate evaporation.

This work investigates an alternate sample-preparation method for the rapid determination of 14 analytes in solar-grade silicon wafers that contributes minimal contamination using an ELAN DRC II ICP-MS with patented dynamic band-pass tuning (DBT) technology.

Experimental

Problematic Interferences

ICP-MS is known to be one of the most accurate techniques for ultratrace elemental analysis. However, spectral interferences can originate from polyatomic and isobaric ions which result from plasma and/or matrix species. When introducing a silicon matrix, the most-often-observed solvent-related and silicon-based interferences from interactions with the plasma are shown in Table 1.

Table 1. **Solvent-related and silicon-based interferences.**

m/z	Interference	Analyte
31	^{30}SiH, $^{14}N^{16}OH$	P
39	^{38}ArH	K
47	^{28}SiF, $^{30}SiOH$	Ti, PO
48	^{29}SiF, $^{28}SiFH$	Ti
56	$^{40}Ar^{16}O$	Fe
60	$^{28}Si^{16}O_2$	Ni
63	$^{29}Si^{16}O_2H$, $^{28}Si^{16}OF$	Cu
64	$^{29}Si^{16}OF$, $^{28}Si^{16}OFH$	Zn
65	$^{30}Si^{16}O_2H$, $^{30}Si^{16}OF$	Cu
66	$^{29}SiF_2$, $^{30}Si^{16}OFH$	Zn
68	$^{40}Ar\,^{28}Si$, $^{30}SiF_2$	Zn

Dynamic Reaction Cell Technology

While cold plasma has been shown to be effective at reducing argon-based interferences, it is much more prone to matrix suppression than hot plasma. Additionally, because of the low plasma energy, other polyatomic interferences, which are not seen under hot-plasma conditions, may be preferentially formed. Collision cells using multipoles and non-reactive gases have proven useful in reducing polyatomic interferences. This approach necessitates the use of kinetic energy discrimination (KED) to remove the unwanted by-products. However, kinetic energy discrimination results in a significant loss of analyte sensitivity, which is an issue when analyzing at sub-ppbw levels. Additionally, the sensitivity loss is more significant for lighter analytes when using KED.

The Dynamic Reaction Cell (DRC) uses a technique called chemical resolution to remove the interferences. The DRC is a pressurized quadrupole positioned before the analyzer quadrupole. A highly reactive gas, such as pure ammonia, is supplied to the cell, where specific ion-molecule chemistry occurs. The advantage of this configuration is that ions of a specific mass range pass through the cell, while ions outside of this range are ejected from the cell. This process is known as dynamic bandpass tuning (DBT). With this patented technology, the ELAN DRC II ICP-MS does not need to use cold plasma and also avoids the use of KED since chemical resolution is used to remove the interferences. As a result of this capability, undesirable by-product ions do not form within the cell – even when very reactive gases such as NH_3 and O_2 are used. Another advantage of the ELAN DRC II ICP-MS is that it always operates under robust hot-plasma conditions, effectively decomposing the sample matrix and eliminating the need for matrix-matched standards or the method of standard additions (MSA). The instrument also has the ability to combine elements run in DRC mode (with reaction gas) with elements run in standard mode (without reaction gas) in a single analytical method, thereby eliminating the need to analyze the sample twice or under two different plasma conditions.

Table 2 shows the operating conditions of the ELAN DRC II ICP-MS used for the ultratrace interference-free analysis of solar-grade silicon wafers.

Table 2. **Operating conditions for ELAN DRC II ICP-MS.**

Parameter/System	Setting/Type
Nebulizer	PFA concentric type
Spray chamber	PFA Scott-type double-pass
Torch	Quartz
Torch injector	2 mm i.d. Pt
Sampler cone	Pt
Skimmer cone	Pt
RF power	1500 W
Plasma gas flow	16 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer gas flow	0.96 L/min
Sample uptake rate	100 µL/min
Integration time	1 sec/mass
Replicates	3 or 7*

For calculation of method detection limits (MDLs).

Sample Preparation

Solar-grade silicon-wafer samples with impurities above the 6N level (LDK Solar Co., Ltd, Xinyu, Jiangxi, China) were used for the method development in this work. A class-100 clean-room facility was utilized for the handling and dissolution of the silicon wafers. Prior to digestion, the wafers were etched by wash solutions to remove the first few surface layers which are not representative of the bulk silicon. SEMI-grade ultrapure HNO_3 and HF were used for digestion (Tamapure-AA 10, TAMA Chemicals, Japan) in capped PFA bottles. The silicon-matrix concentration was adjusted to 1000-2000 ppm (mg/L) using ultrapure water. These samples were then analyzed directly by ICP-MS in the clean room for 13 analytes, including boron.

The oxidation of phosphorus inside the Dynamic Reaction Cell (DRC) has shown to be an effective method of improving the phosphorus detection limit compared to classical ICP-MS analysis.[4] When introducing a silicon-matrix solution for quantitative ultratrace elemental analysis by ICP-MS, the silicon and HF in the solution will form the $^{28}Si^{19}F$ polyatomic ion, which overlaps with $^{31}P^{16}O$. In order to determine phosphorus (as $^{31}P^{16}O$) at mass 47, complete elimination of silicon from the sample solution is necessary. Since phosphorus is much less volatile than boron, a more aggressive heating procedure can be used to remove the silicon. A major benefit of such a sample-preparation method is the reduced level of operator skill required compared to other methodologies. The digested silicon solutions were split. For the determination of phosphorus, the samples were heated to near dryness on a hot plate. Several drops of concentrated HF were then added to the residues and heated to near dryness again. These steps were repeated two more times, with the final residues dissolved in 5% HF (v/v) for analysis.

Calibration Standard Solution

The calibration blank solution for 13 elements contained 4% HF/6% HNO_3 (w/w), which is the same proportion used for preparation of the silicon wafers. The calibration-blank solution for phosphorus contained 5% HF (v/v). Calibration standards were prepared from a multi-element stock solution (PerkinElmer Pure, Shelton, CT, USA). A 1000 ppm (mg/L) silicon solution spiked with a 1 ppb (µg/L) multi-element standard was used for the AutoLens calibration. The AutoLens calibration was repeated one more time right after running the external calibration curve, which guaranteed the robust instrumental performance and assured the accuracy on the analysis of this work.

Results and Discussions

Spike Recoveries

To validate the sample-preparation methodology, spike recoveries were performed in samples containing different concentrations of silicon. Figure 1 (Page 5) shows 500 ppt spike recoveries of 13 analytes in a silicon matrix which varied from 100-5000 ppm (mg/L). The results indicate that samples containing up to 2000 ppm (mg/L) silicon can be analyzed against simple external calibration curves which do not contain any silicon. It is also worth noting that the analyte-signal suppression is less than 20%, which is excellent for this matrix type.

Stability

Since silicon is a refractory element, it tends to form oxides in the plasma, particularly when cold-plasma conditions are used. These silicon oxides deposit on the surface of the interface cones, causing significant signal drift. The ability of the ELAN DRC II ICP-MS to use hot-plasma conditions for all analytes should greatly reduce this signal drift. Figure 2 (Page 5) shows two-hour stability of a 1000 ppm (mg/L) silicon solution spiked with 500 ppt (ng/L) of all analytes (phosphorus data was obtained in a 5% HF solution). The sample solution was continuously aspirated without rinse. Both DRC and standard mode elements were determined in the same multi-element run with a total measuring time (for 3 replicates) of less than 3 minutes per sample. The results highlight the suitability of the ELAN DRC II for the routine quantification of ultratrace impurities in solar-grade silicon wafers.

Figures of Merit

Since matrix-matched calibration curves are not required to analyze silicon-wafer samples, the detection limits achieved on the ELAN DRC II ICP-MS are independent of the sample matrix and can be determined from the simple acid calibration blank.

Table 3 shows the figures of merit obtained from this new sample-preparation methodology, including method detection limits (MDLs), background equivalent concentrations (BECs), spike recoveries, and stabilities. The MDLs were calculated by multiplying the standard deviation of the 4% HF/6% HNO_3 (w/w) calibration blank (used for preparation of silicon wafers) by three and dividing by the net sensitivity of the 13 elements in 4% HF/6% HNO_3. The BECs were calculated by measuring their signal intensities in 4% HF/6% HNO_3 and dividing them by the net analyte sensitivities in 4% HF/6% HNO_3. MDLs and BECs for phosphorus were obtained using the 5% HF (v/v) calibration blank.

Table 3. **Method detection limits (MDLs), background equivalent concentrations (BECs), spike recoveries and 2-hour stability at 500 ppt (ng/L) level for 13 analytes in a 1000-ppm silicon-matrix solution (P and PO data were obtained in 5% HF).**

Analytes	m/z	Mode	BECs (ng/L)	MDLs (ng/L)	500-ppt Recovery %	2-hour Stability %
B	11	Standard	24	10	92	1.7
Al	27	Standard	0.6	0.4	102	1.9
P	31	DRC	2337	240	95	3.5
Ca	40	DRC	1.4	0.7	114	3.7
PO	47	DRC	1040	20	113	4.4
Ti	50	DRC	0.4	0.6	99	3.1
Cr	52	DRC	1.8	1.3	96	3.7
Mn	55	DRC	0.4	0.4	82	3.7
Fe	56	DRC	2.3	0.2	118	4.1
Ni	58	DRC	2.9	1.7	87	4.6
Cu	63	DRC	1.3	1.5	91	4.7
Zn	64	DRC	13.7	1.0	113	3.1
As	75	Standard	6.7	2.7	106	3.3
Ag	107	Standard	0.5	0.6	87	4.5
Au	197	Standard	0.03	0.06	94	3.9

Table 4. **Ultratrace analyte determination in a solar-grade silicon-wafer sample (above 6N), indicating the difference between two sample preparation methods – conventional and the one proposed in this work. All units were ng/g (ppbw) in solid (PO calculated as P). Mean of three replicates.**

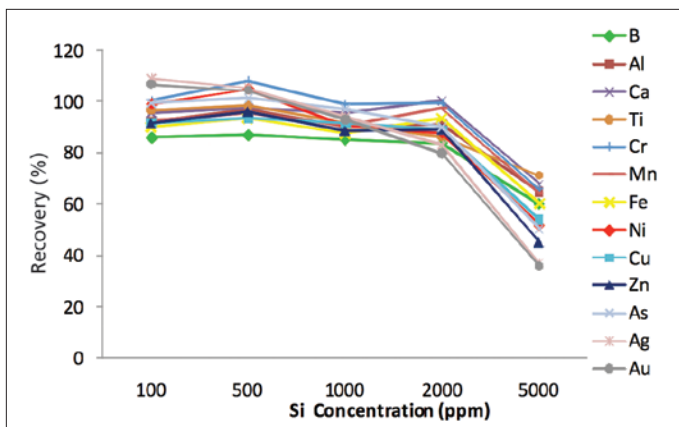| Analytes	m/z	Conventional Method (ng/g)	New Method (ng/g)
B	11	29	32
Al	27	2	1
P	31	N.D.	N.D.
Ca	40	21	14
PO	47	103	89
Ti	50	N.D.	N.D.
Cr	52	1	2
Mn	55	6	1
Fe	56	34	24
Ni	58	30	14
Cu	63	10	5
Zn	64	N.D.	N.D.
As	75	12	5
Ag	107	17	6
Au	197	N.D.	N.D.

N.D.: less than MDL

Figure 1. Silicon matrix effect on the spike recoveries of 13 analytes in 100-5000 ppm (mg/L) silicon.
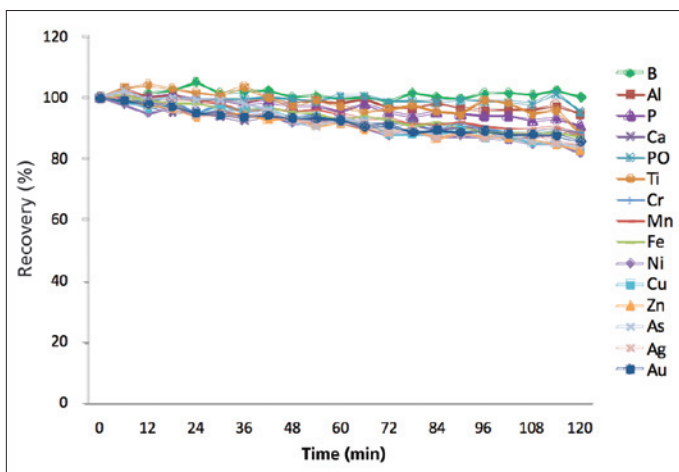

Figure 2. A 2-hour stability of all analytes spiked at 500 ppt (ng/L) level in a solution of 1000 ppm (mg/L) silicon (PO data was obtained in 5% HF). Solution was continuously aspirated without rinse. Both DRC and standard-mode elements were determined in the same multi-element run with a total measuring time (for 3 replicates) of less than 3 minutes per sample.

Case Study

In order to validate this new methodology as a total solution for the solar-cell industry, a solar-grade silicon-wafer sample was divided into six pieces, with three pieces prepared by each of the two sample-preparation methods (i.e. direct analysis and the conventional procedure) and then analyzed by ICP-MS. The mean results for the three pieces are shown in Table 4 (Page 4). All units are ng/g in the solid (PO calculated as P). Using the new methodology, the reagent-blank levels were generally lower than those obtained by the conventional methodology. As a result, the analyte concentrations were also lower, particularly for P, Fe, Ni and Ag, using the new sample-preparation method. Thus, the difference between the two sample-preparation methods highlights the accuracy of ELAN DRC II ICP-MS for the determination of impurities in solar-grade silicon wafers and the suitability of the proposed methodology to meet specific customer needs.

Conclusion

The ELAN DRC II ICP-MS provides ultratrace, interference-free analysis of solar-grade silicon wafers. It is the appropriate tool for obtaining accurate, sub-ppb (µg/L) level results quickly using a new, relatively simple sample-preparation method. This technology can be a major benefit to laboratories because it can be readily and easily used without time-consuming changes to instrumental operating conditions.

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