Ultratrace Analysis of Solar (Photovoltaic) Grade Bulk Silicon by ICP-MS

Application Note

Semiconductor

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Abstract

A new quantitative method for the determination of ultratrace elemental impurities present in photovoltaic grade silicon is described using the Agilent 7500cs ICP-MS. Boron (volatile element) and phosphorus (subject to Si-based interferences) are of particular importance to the industry; therefore, special attention was given to the sample pretreatment stage in order to analyze these elements by ICP-MS. Good recovery results for all elements validated the sample preparation strategy. Example data for a range of elements present in 13 different Si samples is presented, along with a list of detection limits. B and P can be determined at the low ppb level in the solid and other elements studied can be measured at the ppt level.

Introduction

Research into alternative energy sources is accelerating with one of the most dynamic areas of interest being the development of devices to harness solar energy. According to the "solar grand plan," 69% of total electricity in the USA could be sourced from solar power by 2050 (*Scientific American*, January 2008). The growing demand for solar power devices requires highly efficient energy converters, principally silicon. Impurity control of solar (or photovoltaic) grade silicon, particularly for boron and phosphorus, is critical to the efficiency of the finished device. Historically the analysis of phosphorus has been performed by inductively coupled plasma optical emission spectroscopy (ICP-OES), but with a demand for lower detection limits (DLs), a more sensitive method is needed. This work describes the sample preparation and analysis of 31 analytes in bulk silicon (used for the manufacture of solar silicon devices) using an Agilent 7500cs inductively coupled plasma mass spectrometer (ICP-MS).

Analytical Challenges

The latest industry requirement for impurity levels in silicon is lower than 10 ppb in the solid. Boron and phosphorus are of particular importance but are difficult elements to analyze by ICP-MS. In a Si matrix, the polyatomic ion $^{30}Si^{1}H$ interferes with ^{31}P. An alternate strategy is to determine P indirectly by measuring $^{31}P^{16}O$ at mass 47, but here $^{28}Si^{19}F$ also interferes (see Recovery Test section for more detail). Boron is a volatile element that is easily lost during the sample preparation stage. It is critical, therefore, that a new method removes Si for the determination of P, while avoiding the loss of B.

Silicon Sample

Pieces of silicon taken from a block of silicon were analyzed for the following analytes: Li, B, Na, Mg, Al, K, Ca, P, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Sr, Zr, Nb, Mo, Cd, Sn, Sb, Ba, Ta, W, Pb, Th, and U. The method can also be applied to polysilicon granules or chips.

Sample Preparation

Two sample preparation procedures were followed: one for the analysis of all elements except boron, and a slightly modified procedure for boron. First, the sample surface was cleaned with HF. The sample pieces were then dissolved in HF/HNO_3. A small aliquot of H_2SO_4 was added, except to samples being prepared for boron analysis (the higher temperature generated during the evaporation of the H_2SO_4 solution would result in the loss of volatile boron). Sample solutions were heated to near dryness, and then dissolved in 0.5% v/v HNO_3.

Calibration Standard Solution

The calibration blank solution contained 0.34% (w/w) HNO_3 and 0.33% (w/w) H_2SO_4 . Calibration standards were prepared by spiking the blank solution with a multielement standard solution (Spex, Metuchen, NJ, USA) at the following concentrations: 0, 0.1, 0.2, 0.5, and 1 ppb.

Instrumentation

An Agilent 7500cs ICP-MS with Octopole Reaction System (ORS) was used throughout the study. The sample introduction configuration included an Agilent Micro Flow 100 nebulizer, inert PFA spray chamber with sapphire torch injector, and platinum sampling cone and skimmer cone with a brass skimmer base. An Agilent Integrated Autosampler (I-AS) with tray type F sample vials was used. Instrument operating conditions are given in Table 1.

Table 1. Agilent 7500cs ICP-MS Operating Parameters

			Method step (stabilization time)	
		Step 1 (5 sec)	**Step 2 (45 sec)**	**Step 3 (30 sec)**
Parameter	**Unit**	**Cool**	**No gas**	**He**
RF power	W	600	1600	1600
Sampling depth	mm	20	8	8
Carrier gas	L/min	0.8	0.8	0.8
Makeup gas	L/min	0.8	0.46	0.46
ORS He gas	mL/min	0	0	5
Analytes		^{7}Li, ^{23}Na	^{11}B, ^{138}Ba	^{47}Ti, ^{52}Cr
		^{24}Mg, ^{27}Al	^{181}Ta	^{59}Co, ^{60}Ni,
		^{39}K, ^{40}Ca	^{182}W	^{68}Zn, ^{75}As
		^{45}SiO, ^{47}PO		^{88}Sr, ^{90}Zr
		^{55}Mn, ^{56}Fe		^{93}Nb, ^{95}Mo
		^{63}Cu, ^{71}Ga		^{111}Cd, ^{118}Sn
				^{121}Sb, ^{208}Pb
				^{232}Th, ^{238}U

Notes: The purity of the He cell gas used was >99.995%. Sample uptake time was 60 sec and rinse time between samples was 60 sec. Integration time was 0.66 sec × 3 points for all elements with the exception of: ^{45}SiO (1 sec × 3 points), ^{75}As (2 sec × 3 points), ^{47}Ti (3 sec × 3 points), and ^{47}PO (5 sec × 3 points). Total analysis time per sample (3 replicates) was 9 min.

Recovery Test

When silicon is dissolved in HF/HNO_3, a significant amount of silicon remains in solution, even after heating. Phosphorus determination at mass 31 is normally performed in helium collision mode. However, any Si present in solution creates ^{30}SiH in the plasma, which interferes with ^{31}P; $^{14}N^{16}OH$ also overlaps at mass 31. Another approach for the determination of P is to measure the PO polyatomic ion at mass 47, which can be produced using cool plasma conditions (reduced plasma power). In this case the background equivalent concentration (BEC) for P is very low at 20 ppt. Although Ti has an isotope at mass 47, it is not ionized under cool plasma conditions, so there is no Ti interference on PO. Conversely, Ti can be measured using He collision mode under normal plasma conditions as PO does not form in a hot plasma. Using a combination of measurement modes, both PO and Ti can be determined effectively. It is worth noting that because any Si remaining in solution with HF would give rise to $^{28}Si^{19}F$, which interferes with $^{31}P^{16}O$, complete elimination of Si from the sample solution is absolutely necessary in order to determine phosphorus, regardless of the measurement mode used. This is achieved by the addition of H_2SO_4. However, when heating the sample solution with H_2SO_4, the high temperature results in the loss of boron as BF_3. Therefore a slightly modified, lower temperature sample prep, without the addition of H_2SO_4 (as complete removal of the silicon matrix is not required), is used for boron. A recovery test was performed to validate this sample preparation strategy.

As significant inhomogeneity in the Si block was observed for Fe, Mn, and Ni, the recovery test was performed by dissolving a larger amount of sample to make a bulk solution: 2.0 g of sample was dissolved in 25 mL HF and 25 mL HNO_3 in a 250-mL PFA beaker. A further 15 mL of HF and 15 mL of HNO_3 were added, the beaker was capped, and the solution was left overnight. Six 10-mL aliquots of the bulk solution were transferred to PFA beakers A, B, C, D, E, and F. Beakers G and H were left empty (for reagent blanks). 0.5 mL of 1:10 H_2SO_4 was added to beakers A, B, C, and G. Beakers C and F were spiked with 75 µL of 1 ppm standard solution. All the solutions were heated for approx 2 hours. After cooling, 0.5 mL of 1:10 H_2SO_4 was added to beakers D, E, F, and H in order to match the acid matrix. Then the residue was dissolved in 1:200 HNO_3 and analyzed. To confirm the efficiency of matrix removal, silicon (^{28}Si) was determined by H_2 reaction mode. Concentrations in solution (ppb) are shown in Table 2 and Figure 1.

Table 2.. Concentrations in Solution (ppb) and Recovery Data for 5-ppb Spikes Added to Si Samples Prepared With and Without the Addition of H_2SO_4 (Note: Reagent blank is the mean value from beakers G and H.)

			H_2SO_4 added				**No H_2SO_4 added**		
	Reagent blank	**A**	**B**	**C**	**Recovery (%)**	**D**	**E**	**F**	**Recovery (%)**
7 Li	0	0	0	5	100	0	0.0012	5.3	110
11 B	0.0051	0.021	0.03	0.086	1	0.083	0.06	5	99
23 Na	0.023	0.31	0.61	5.8	110	1.3	1.6	7.4	120
24 Mg	0.0011	0.52	0.95	5.6	98	0.7	0.72	5.3	92
27 Al	0.0062	0.19	0.44	5.1	95	0.62	0.37	4.8	87
28 Si	0.11	0.28	0.55	0	—	450	14000	25000	—
39 K	0.012	0.09	0.17	5.2	100	0.31	0.37	8.9	170*
40 Ca	0.0091	0.38	0.81	5	88	0.77	0.96	5.9	100
$^{31}P^{16}O$	0	0.026	0.096	4.2	84	3	90	190	3000
47 Ti	0	0.056	0.14	5.4	110	0.13	0.19	5.4	100
52 Cr	0	0.003	0.0068	5.4	110	0.0048	0.016	4.8	97
55 Mn	0	0	0.0014	4.9	97	0.0023	0.0015	4.5	89
56 Fe	0.0024	0.048	0.12	4.9	96	0.31	0.12	4.7	89
59 Co	0	0	0.0011	5.4	110	0.0011	0.0011	5.2	100
60 Ni	0	0.022	0.038	5.5	110	0.035	0.036	5.2	100
63 Cu	0	0.0064	0.015	4.8	95	0.018	0.041	5.1	100
68 Zn	0.0044	0.022	0.043	5.3	110	0.048	0.047	5.5	110
71 Ga	0	0	0	5	100	0	0	5.2	100
75 As	0	0.0016	0.0029	5.1	100	0.0028	0.0024	5.1	100
88 Sr	0	0.0065	0.012	5.4	110	0.056	0.064	5.2	100
90 Zr	0	0	0	5.3	110	0.0021	0	5.2	100

*Poor recovery probably due to contamination

(Continued)

Table 2. Concentrations in Solution (ppb) and Recovery Data for 5-ppb Spikes Added to Si Samples Prepared With and Without the Addition of H_2SO_4 (Note: Reagent blank is the mean value from beakers G and H.) (continued)

		H_2SO_4 added				No H_2SO_4 added			
	Reagent blank	**A**	**B**	**C**	**Recovery (%)**	**D**	**E**	**F**	**Recovery (%)**
93 Nb	0	0	0.0017	5.3	110	0.0045	0.0048	5.2	100
98 Mo	0	0.0018	0.0013	5.3	110	0.0006	0.046	5.2	100
111 Cd	0	0	0	5.4	110	0	0	5.5	110
118 Sn	0.0015	0.0023	0.005	5.4	110	0.0045	0.0056	5.4	110
121 Sb	0	0	0	5.3	110	0.0024	0.002	5.4	110
138 Ba	0	0.001	0.0022	5.6	110	0.0044	0.0041	5.6	110
181 Ta	0	0.043	0.075	5.5	110	0.11	0.2	4.9	95
182 W	0	0.032	0.071	5.7	110	0.053	0.063	5.6	110
208 Pb	0	0.0012	0.0021	5.6	110	0.0036	0.0032	5.8	120
232 Th	0	0	0	5.8	120	0	0	6	120
238 U	0	0	0	5.9	120	0	0	6.1	120

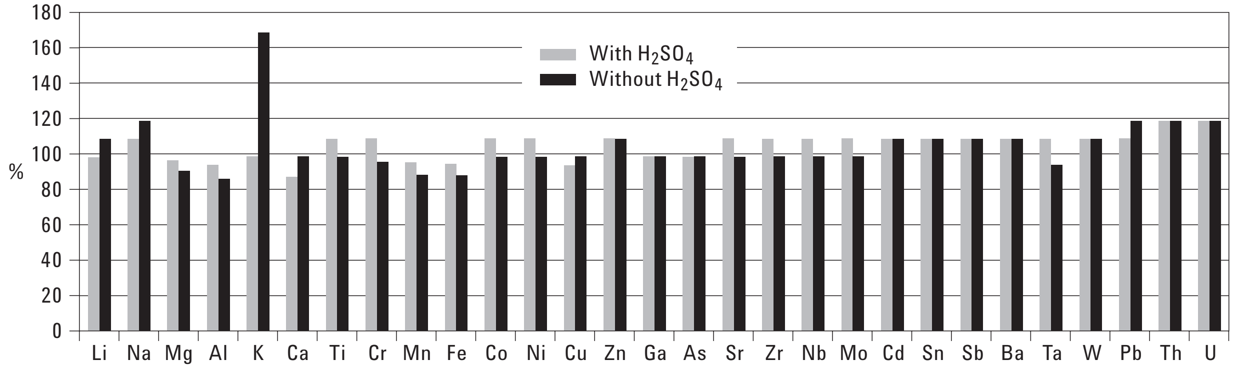

Figure 1. Recovery of 5-ppb spikes added to sample solution.

From the recovery test results (Table 2 and Figure 1), it can be concluded that the addition of sulfuric acid removes the silicon matrix completely (as well as boron), due to the higher temperature evaporation process, which makes it possible to determine phosphorus at the low ppb level in the solid. The results also show that a simple evaporation without sulfuric acid is effective for the determination of boron. Although it has been reported that the addition of mannitol stabilizes boron in solution, acceptable recoveries can be obtained without the addition of mannitol, provided high solution temperatures are avoided. With no H_2SO_4 added, it is important to closely monitor the evaporation of the sample. If the sample is allowed to evaporate to dryness, Nb, Ta, W, and Au will be lost. The concentration of silicon remaining in the non-H_2SO_4 prep solution was 10 to 20 ppm.

Detection Limits

Three sigma detection limits (DLs) were calculated from the calibration curves as shown in Table 3. DLs in the solid were obtained by multiplying the solution DL by 50 (0.3 g made up to 15 mL).

Table 3. Detection Limits (3 s) in Solution and in the Solid. All Units: ppt

	ng/L in solution	ng/kg in solid
7 Li	0.011	0.55
11 B	20	1000
23 Na	0.78	39
24 Mg	0.16	8
27 Al	0.56	28
39 K	0.13	6.5
40 Ca	4.3	215
47 PO	17	850
47 Ti	2.2	110
52 Cr	1.3	65
55 Mn	0.067	3.35
56 Fe	0.8	40
59 Co	0.015	0.75
60 Ni	0.21	10.5
63 Cu	0.31	15.5
68 Zn	4.6	230
71 Ga	0.080	4
75 As	0.13	6.5
88 Sr	0.037	1.85
90 Zr	0.11	5.5
93 Nb	0.046	2.3
98 Mo	0.27	14
111 Cd	0.24	12
118 Sn	0.4	20
121 Sb	0.26	13
138 Ba	0.093	4.65
181 Ta	0.058	2.9
182 W	0.34	17
208 Pb	0.42	21
232 Th	0.16	8.2
238 U	0.014	0.7

Quantitative Analysis

Samples taken from 13 different polysilicon blocks were analyzed by ICP-MS. The concentration data for elements present in the different samples are shown in Table 4. Concentrations are expressed as ppb in the original solid. Note the inhomogeneity for elements such as Fe, Mn, and Ni.

Conclusions

Ultratrace elemental impurities in solar grade silicon can be quantitatively analyzed following an appropriate sample pretreatment stage and measurement by the Agilent 7500cs ICP-MS. The sample preparation detailed in this report is quite simple and reproducible. B and P can be determined at the low ppb level in the solid and other elements studied can be measured at the ppt level.

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Table 4. Quantitative Data (ppb in the Original Solid) for Samples Taken from 13 Different Polysilicon Blocks

	#A	**#B**	**#C**	**#D**	**#E**	**#F**	**#G**	**#H**	**#I**	**#J**	**#K**	**#L**	**#M**
7 Li	0.067	0.097	0.077	0.057	0.26	0.051	0.049	0	0.012	0.098	0.11	0.1	0.076
11 B	62	62	100	13	21	39	29	14	6.8	12	6.1	10	9.3
23 Na	2.8	15	2.5	6.2	450	0	2.5	28	17	0	25	61	140
24 Mg	1.9	3.8	3.1	0	0	0	0	0	0	0	1.6	0	0
27 Al	100	100	270	130	130	150	170	43	39	86	120	110	150
39 K	1.4	3.5	1.1	4.2	210	0.41	3.7	14	7.5	0.83	5.3	11	3
40 Ca	6.8	5.5	9	0	56	0	0	20	0	0	0.57	2.5	0.63
$^{31}P^{16}O$	64	59	70	61	99	97	110	25	41	110	91	87	110
47 Ti	0	2.5	310	0	0	0	0	0	0	2.9	8.7	2.9	1.3
52 Cr	0.34	0.64	16	1.1	2.1	0	0	2.4	1.2	1	0.61	0.18	1.1
55 Mn	0.022	0.027	3.4	0.31	0.32	0	0	0.16	0.87	0.017	0.061	0.21	0.078
56 Fe	5.7	5.1	1700	42	29	3.5	4.9	36	140	3	3.7	32	10
59 Co	0.28	0.19	7.6	0.35	1.6	0.21	0.33	3.3	0.35	0.036	0.087	0.054	0.1
60 Ni	13	2.5	270	6.1	16	17	18	21	12	1.4	3.3	2.3	12
63 Cu	1.6	2.8	40	5.2	24	2.6	6.1	39	4.5	2.2	3.9	1.9	2.1
68 Zn	0.3	0.073	0.015	1.8	41	0	0	7.4	3.3	0	0.47	4.1	0
71 Ga	0.077	0.11	0.28	0.1	0.14	0.073	0.07	0	0.016	0.096	0.11	0.11	0.099
75 As	0.18	0.22	0.17	0.17	0.2	0.01	0	0.28	0.22	0.086	0.086	0.07	0.034
88 Sr	0.017	0.013	0.071	0.022	0.23	0	0	0.19	0.077	0.014	0.027	0.057	0.074
90 Zr	0.028	0.04	13	0.15	0.32	0	0	0.28	0.11	0	0	0.037	0.027
93 Nb	0	0.012	2	0	0	0	0	0.064	0	0.013	0.027	0.011	0.27
95 Mo	0.092	0.55	5.4	0.032	0	0	0	3.7	0.6	0	0.39	0.048	10
111 Cd	0	0.016	0	0	0	0	0	0	0	0	0.023	0.023	0
118 Sn	2.3	11	0.18	9.6	11	2.7	2.6	0.55	0.074	7.9	9	7.7	2.4
121 Sb	0.42	1.1	0.038	1	1.2	0.39	0.34	0.6	0.32	0.81	0.97	0.8	0.36
138 Ba	0.029	0.039	0.25	0	0.15	0	0	5.6	0.57	0.12	0.17	0.11	0.029
181 Ta	0	0	0.52	0	0.91	0	0	0	0	0	0	0.013	0.033
182 W	38	34	28	15	12	25	6.8	200	8.4	12	11	14	8.8
208 Pb	0	0.016	0.022	0	1.8	0	0	1	0.4	0.12	0.31	0.45	0.053
232 Th	0	0	0.049	0	0	0	0	0	0	0	0	0	0
238 U	0	0	0.5	0	0	0	0	0	0	0	0	0	0

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