

Comparison of Sector Field ICP-MS and Glow Discharge Mass Spectrometry for the determination of impurities in silicon

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Introduction

The increasing demand for alternative energy sources has fuelled significant research and development in the solar energy sector. The level of impurities in the silicon raw material is crucial since it limits the photovoltaic efficiency of the resulting solar cell.

FIGURE 1. Production site of Sunicon AG in Freiberg (Sachsen), Germany equipped with solar panels



Methods

Sector Field ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and Glow Discharge Mass Spectrometry (GD-MS) are compared for the detection of impurities in silicon. The Thermo Scientific ELEMENT 2 High Resolution Sector Field ICP-MS and the ELEMENT GD High Resolution Glow Discharge Mass Spectrometer were used throughout this study (Figure 2). For Sector Field ICP-MS the following sample preparation protocol was used: After surface cleaning with HF, 0.4 g silicon was dissolved with HF / HNO₃. The solution was heated to near dryness and dissolved in diluted HNO₃ to a final volume of 20 mL. With GD-MS, the samples were directly analyzed after grinding on diamond-bladed discs and cleaning with HNO₃, DI water and isopropanol. Further surface contaminations were removed during the 10 minute pre-sputter period.

FIGURE 2. ELEMENT 2 High Resolution ICP-MS (left) and ELEMENT GD High Resolution Glow Discharge (right) Mass Spectrometers



Results

Polyatomic interferences originating from the sample matrix, the Ar plasma gas, and H and O from the solvent can lead to falsely high results in ICP-MS. Therefore, for accurate results, it is of major importance to reliably remove all interferences. With High Resolution double focusing Sector Field Mass Spectrometers, the analyte signals are resolved from all interferences by their difference in mass. This is shown exemplarily for the ELEMENT 2 ICP-MS (Figure 3) and for the ELEMENT GD (Figure 4). For such scans, 10 times wider than usual mass windows are used in order to show the interferences. For quantitative analysis, smaller mass windows, containing only the analyte peaks, have been chosen. The ELEMENT 2 Limits of Detection (3σ) calculated from replicate measurements of a blank are listed in Table 1 together with the ELEMENT GD data calculated from replicate measurements of a high purity silicon sample.

FIGURE 3. Separation of ³¹P, ⁴⁴Ca, ⁴⁸Ti, ⁵¹V, ⁴⁸Ni and ⁶³Cu from the interferences in Si/HF matrix with the ELEMENT 2

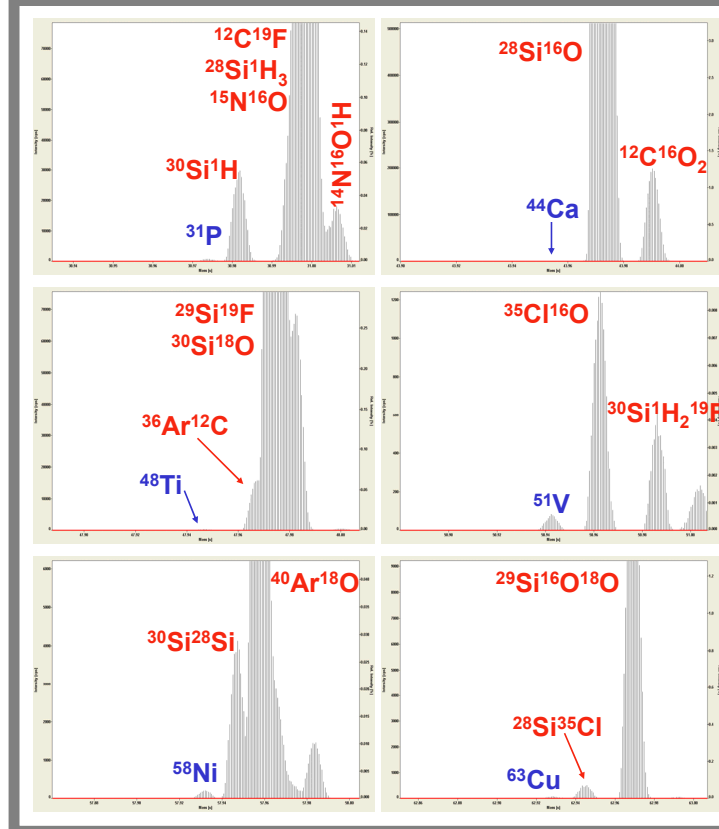
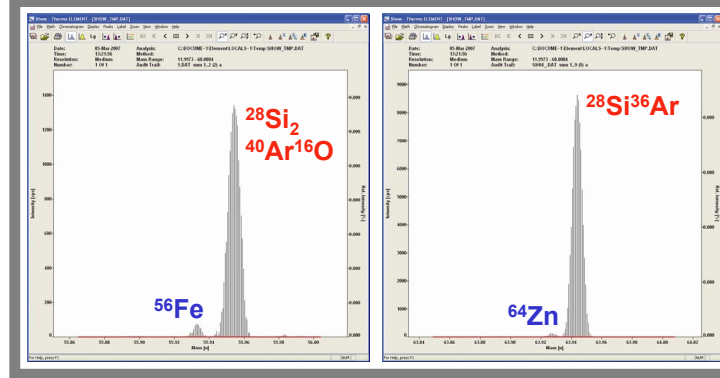


FIGURE 4. Separation of ⁵⁶Fe and ⁶⁴Zn from the interferences in Si with the ELEMENT GD



Conclusions

With both High Resolution Mass Spectrometers ELEMENT 2 and ELEMENT GD the analyte signals are reliably resolved from all interferences. This is necessary to ensure accurate results. For most elements, the limits of detection for the ELEMENT GD are in the sub ppb range for silicon samples. The major limitation here is the signal to noise ratio, with a matrix sensitivity of typically 5 x 10⁹ cps ²⁸Si in Medium Resolution mode (R=4000), and a detector background signal of < 0.5 cps.

With the ELEMENT 2, even lower limits of detection in the silicon material are obtained when removing most of the Si matrix by evaporation. Here the cleanliness of ICP-MS sample preparation is of crucial importance, since it is necessary to dissolve the samples using ultra-high purity acids and containers in a clean-room environment in order to reduce contamination during sample handling.

For both techniques, the matrix related polyatomic interferences have been resolved from the analytes of interest by using Medium and High Resolution. Therefore, it is not necessary to completely remove all Si during preparation of the ICP-MS samples.

For a direct control of the quality of solar cell silicon during the production process, the ELEMENT GD is the instrument of choice, because the samples can be analyzed without a labor intensive and contamination prone sample digestion process. For more research orientated work or for the determination of impurities in semiconductor grade silicon, better limits of detection can be obtained with the described sample preparation procedure and analysis on the ELEMENT 2.

Acknowledgements

We would like to thank Sunicon AG, Freiberg (Sachsen), Germany, for kindly permitting the printing of Figure 1.

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Table 1. Limits of Detection of the ELEMENT 2 and the ELEMENT GD in silicon

	ELEMENT 2 LoD in Solution [ng/L]	ELEMENT 2 LoD in Silicon [ng/g]	ELEMENT GD LoD in Silicon [ng/g]
Li	0.01	0.0005	0.02
Be	0.42	0.02	0.5
B	7	0.4	1.3
Na	0.16	0.008	0.4
Mg	0.12	0.006	0.05
Al	0.5	0.025	0.6
P	2.20	0.11	7
K	0.1	0.005	1.8
Ca	0.83	0.04	2.3
Sc	0.04	0.002	0.1
Ti	0.17	0.009	0.06
V	0.04	0.002	0.03
Cr	0.36	0.018	0.15
Mn	0.04	0.002	0.06
Fe	0.75	0.037	0.5
Ni	0.2	0.01	0.34
Co	0.015	0.001	0.1
Cu	0.27	0.013	0.2
Zn	0.98	0.05	0.5
Ga	0.002	0.0001	1.4
Ge	0.16	0.008	1.5
As	0.15	0.008	0.3
Se	3	0.15	1.3
Rb	3.16	0.16	0.1
Sr	0.04	0.002	0.06
Y	0.05	0.002	0.03
Zr	0.1	0.005	0.11
Nb	0.03	0.001	0.12
Mo	0.17	0.008	0.4
Ru	0.16	0.008	0.2
Rh	0.02	0.001	0.13
Pd	0.09	0.004	0.5
Ag	0.17	0.009	0.2
Cd	0.03	0.002	1.1
In	0.003	0.0002	0.2
Sn	0.06	0.003	0.5
Sb	0.09	0.005	0.3
Te	0.20	0.010	0.7
Cs	0.03	0.002	0.06
Ba	0.08	0.004	0.09
La	0.01	0.0004	0.09
Ce	0.002	0.0001	0.11
Pr	0.003	0.0002	0.04
Nd	0.02	0.001	0.3
Sm	0.02	0.001	0.1
Eu	0.006	0.0003	0.05
Gd	0.002	0.0001	0.12
Tb	0.002	0.0001	0.01
Dy	0.003	0.0002	0.08
Ho	0.001	0.0001	0.05
Er	0.006	0.0003	0.07
Tm	0.005	0.0002	0.02
Yb	0.002	0.0001	0.16
Lu	0.002	0.0001	0.03
Hf	0.09	0.005	0.23
Ta	0.01	0.001	1.8
W	0.07	0.003	0.24
Re	0.003	0.0002	0.03
Ir	0.05	0.003	0.1
Pt	0.14	0.007	0.14
Au	0.16	0.008	0.3
Hg	0.33	0.017	1.1
Tl	0.003	0.0002	0.07
Pb	0.05	0.002	0.08
Bi	0.006	0.0003	0.16
Th	0.0018	0.0001	0.027
U	0.0012	0.0001	0.029