

Analysis of Solar Cell Silicon using Glow Discharge Mass Spectrometry

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Key Words

- ELEMENT GD
- Glow Discharge MS
- Solar Cell Silicon

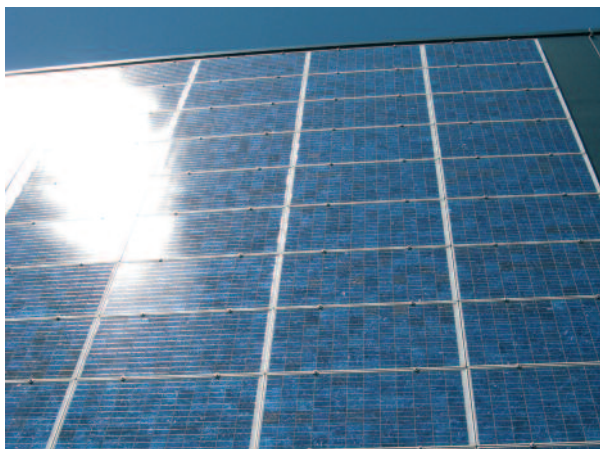


Figure 1: Production site of Deutsche Solar AG in Freiberg (Sachsen), Germany equipped with solar panels.

Introduction

The ever-increasing demand for alternative energy sources has fuelled significant research and development in the entrapment of solar energy through the use of photovoltaic or solar cells. The raw material used in the production of solar cells is bulk crystalline or solar grade silicon. The level of impurities in solar cell silicon is crucial since it limits the photovoltaic efficiency of the resulting solar cell. Rapid and accurate process feedback on impurity levels is therefore crucial in a production environment. The Thermo Scientific ELEMENT GD is the only instrument that can provide short times of less than 20 minutes for the analysis of bulk solar cell silicon directly from the solid material. The ELEMENT GD is capable of determining impurities directly in the solar cell silicon at sub ppb concentration levels for many elements. It is a routine tool that is robust enough to be used in multi-user, multi-shift production facilities. In this particular study, the ELEMENT GD was used to quantify trace element concentrations directly in solar cell silicon. Most elements were analyzed in the most sensitive low resolution mode as no polyatomic interferences were observed. However for many elements, the use of high mass resolution was required to provide accurate results. The results demonstrated that the major spectral interferences originated from polyatomic combinations between the matrix element silicon and the argon discharge gas.

Sample Preparation

The sample preparation method developed for the ultra-trace analysis of bulk solar grade silicon consists of a grinding step, followed by sequential surface cleaning steps with dilute nitric acid, deionized water, and isopropanol. Surface contaminants still remaining on the sample surface are removed during the presputter period. When compared to wet chemical dissolution methods for bulk silicon, the requirement for clean labs, large quantities of ultra-pure mineral acids and water are significantly reduced, therefore minimizing any analytical uncertainties introduced by variable blank levels. Additional advantages to the direct analysis of bulk solar cell silicon include a faster turnaround on results, increased elemental coverage and reduced costs.

Details on sample preparation are listed below:

- Grind Si sample into shape (at least one flat side, min. 20 mm, max. 60 mm diameter)
- Grind sample surface (using grid 220 followed by grid 600 diamond grinding discs; HD Piano, Struers GmbH, Germany)
- Wash surface with DI (deionised) water
- Remove grinding contamination from surface with 10% ultrapure HNO₃
- Wash surface with DI water
- Remove top surface layer with 20% ultrapure HF
- Wash surface with DI water
- Rinse with isopropanol
- Blow dry with Ar stream dry



Instrumental Settings

As a prerequisite of achieving low detection limits, a high signal-to-noise ratio is required. Therefore, the instrument was optimized to give the highest sensitivity for the silicon matrix signal. The highest purity materials for the anode were used throughout since these parts are in direct contact with the glow discharge. The instrumental settings used are listed below:

Discharge current: 65 mA
Discharge voltage: ~ 1000 V
Discharge gas: 400 ml Ar min ⁻¹
Matrix sensitivity: 1 x 10 ¹⁹ cps (Medium Resolution)
Anode material: Steel; anode cap and flow tube: Graphite
Cone: Graphite

The sample introduction system used for the Si measurements is available as a consumables kit for high purity analyses, part no. 1249190 (GD High Purity Kit), the contents of which are listed below:

GD High Purity Kit

- Graphite anode caps (100)
- Graphite flow tubes (100)
- Graphite plug-in cones (100)
- 1 Stainless Steel anode tubes
- 2 Plug-in extraction lenses
- 2 sapphire insulation rings
- 2 Holding rings for Plug-in cones
- 3 O-ring flow tubes
- Clean-room gloves (10)

The graphite anode caps and cones need to be replaced and cleaned after every analysis; the flow tubes are exchanged once or twice a day as required.

The Si loaded parts (anode caps, flow tubes, cones) collected during analysis are cleaned with 10 fold diluted Optima High Purity Hydrofluoric Acid, Fisher Scientific part. no. H/1435/08 in deionised water. After 15 min cleaning in an ultrasonic bath in this 10 fold diluted HF solution, the parts were further ultrasonicated for 5 min in DIW to remove HF. Finally the parts were blown dry with a nitrogen stream, and left to air dry overnight.

Method

The optimum resolution settings, isotopes and measurement time were investigated to achieve ultra-low detection limits at high sample throughput. Major interferences were identified from polyatomic combinations of Si with the discharge gas Ar and Si dimers (Table 1), and the dimer of the matrix element. While the formation rates of ²⁸Si³⁶Ar and ²⁸Si₂ relative to the Si matrix signal were found to be low, they would nevertheless lead to falsely high results for Zn and Fe when applying just nominal mass resolution. Using Medium Resolution however the interferences were completely resolved from the Zn and Fe elemental peaks (Figures 2 and 3).

As a last step in method development, the presputter time was evaluated by monitoring measured concentrations over time. While the matrix signal was stable after several minutes of presputtering, some analytes present at the ppb level (especially Na and Zn) were found to decrease over ~10 minutes due to remaining impurities from surface grinding. The presputter time was therefore set to 12 minutes for all subsequent analyses. With 7 minutes of data acquisition, a total analysis time of 20 minutes was found to provide sufficient sensitivity at the ultra trace level required. Method settings and results are presented in Table 2.

Affected Isotope	Interference
³¹ P	³⁰ Si ¹ H
⁴⁴ Ca	²⁸ Si ¹⁶ O
⁵⁶ Fe	²⁸ Si ²⁸ Si
⁵⁸ Ni	³⁰ Si ²⁸ Si
⁶⁴ Zn	²⁸ Si ³⁶ Ar
⁶⁶ Zn	²⁸ Si ³⁶ Ar
⁶⁸ Zn	³⁰ Si ³⁶ Ar
⁶⁸ Zn	³⁰ Si ³⁶ Ar
⁶⁸ Zn	²⁸ Si ⁴⁰ Ar
⁷⁴ Ge	³⁸ Ar ³⁶ Ar

Table 1: Major interferences.

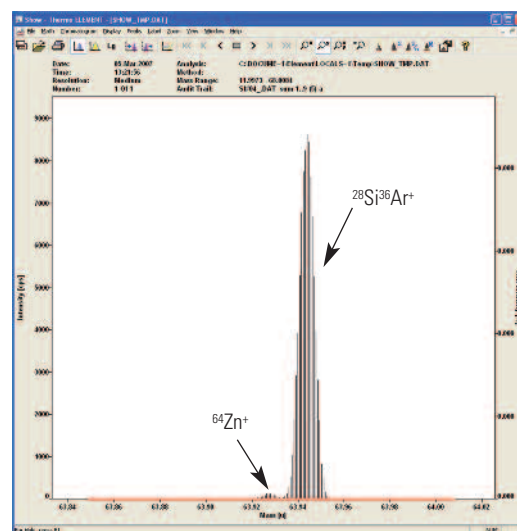


Figure 2: Medium Resolution scan (R = 4000) of ⁶⁴Zn⁺ resolved from ²⁸Si³⁶Ar⁺.

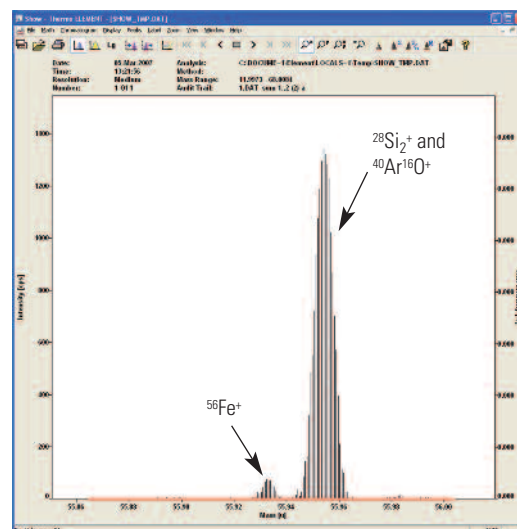


Figure 3: Medium Resolution scan (R = 4000) of ⁵⁶Fe⁺ resolved from ²⁸Si₂⁺.

Element	Mass	Resolution	Average n = 5 spots conc. [ppb]	LoD (3s) n = 5 spots conc. [ppb]
Li	7	LR	< LoD	0.02
Be	9	MR	< LoD	0.5
B	11	MR	2.8	1.3
Na	23	LR	0.6	0.4
Mg	24	MR	0.08	0.05
Al	27	MR	0.8	0.6
P	31	MR	16	7
K	39	HR	2.1	1.8
Ca	44	MR	< LoD	2.3
Sc	45	MR	< LoD	0.10
Ti	48	MR	< LoD	0.06
V	51	MR	< LoD	0.03
Cr	52	MR	0.21	0.15
Mn	55	MR	< LoD	0.06
Fe	56	MR	< LoD	0.5
Ni	58	MR	< LoD	0.34
Co	59	MR	0.4	0.1
Cu	63	MR	0.5	0.2
Zn	64	MR	3.7	0.5
Ga	71	HR	< LoD	1.4
Ge	72	HR	< LoD	1.5
As	75	MR	0.4	0.3
Se	82	MR	< LoD	1.3
Rb	85	MR	< LoD	0.1
Sr	88	MR	< LoD	0.06
Y	89	MR	< LoD	0.03
Zr	90	MR	< LoD	0.11
Nb	93	MR	< LoD	0.12
Mo	95	MR	< LoD	0.4
Ru	102	MR	< LoD	0.20
Rh	103	MR	< LoD	0.13
Pd	105	MR	< LoD	0.5
Ag	107	MR	< LoD	0.2
Cd	111	MR	< LoD	1.1
In	115	MR	< LoD	0.2
Sn	118	HR	< LoD	0.5
Sb	123	MR	< LoD	0.3
Te	126	MR	< LoD	0.7
Cs	133	MR	< LoD	0.06
Ba	138	MR	< LoD	0.09
La	139	MR	< LoD	0.03
Ce	140	MR	< LoD	0.11
Pr	141	MR	< LoD	0.04
Nd	142	MR	< LoD	0.3
Sm	152	MR	< LoD	0.1
Eu	153	MR	< LoD	0.05
Gd	158	LR	< LoD	0.12
Tb	159	LR	0.02	0.01
Dy	164	LR	< LoD	0.08
Ho	165	MR	< LoD	0.05
Er	166	LR	< LoD	0.07
Tm	169	MR	< LoD	0.02
Yb	173	MR	< LoD	0.16
Lu	175	LR	< LoD	0.03
Hf	178	LR	< LoD	0.23
Ta	181	LR	5.3	1.8
W	184	LR	< LoD	0.24
Re	187	LR	< LoD	0.03
Os	189	LR	< LoD	0.35
Ir	193	LR	< LoD	0.10
Pt	195	LR	< LoD	0.14
Au	197	LR	< LoD	0.3
Hg	202	LR	< LoD	1.1
Tl	205	LR	< LoD	0.07
Pb	208	LR	0.09	0.08
Bi	209	LR	< LoD	0.16
Th	232	LR	< LoD	0.027
U	238	LR	< LoD	0.029

Table 2: Results and detection limits obtained for analyse of bulk solar cell silicon at five different spots. LR = Low Resolution, R = 400; MR = Medium Resolution, R >= 4000, HR = High Resolution, R >= 10000.

Results

All results given were measured as ion beam ratios and converted to bulk concentrations by applying the respective calibration factor from the ELEMENT GD's Standard RSF table. This approach is common practice in GD-MS analysis, yielding semiquantative results that typically fall within 30% of the true values. Due to the lack of certified low-level silicon reference materials, all data shown in Table 2 are therefore semiquantitative results.

From the analysis of the purest material available, an estimate of detection limits can be obtained from repeat analysis at 5 different spots (Table 2).

Typically the detection limits achieved are sub ppb, and are limited by the signal to noise ratio of approximately 0.2 cps vs. 1×10^{10} cps (background noise versus matrix sensitivity in Medium Resolution) that gives a theoretical value of 20 ppt. Elements that yield higher detection limits generally suffer from lower isotopic abundances of the isotopes that had to be used, e.g. ^{44}Ca , ^{82}Se , and ^{111}Cd .

While the average values presented in Table 2 were calculated from the standard deviation of 5 spots, the precisions of the individual spots have been omitted for reasons of clarity. As a general rule, the precision obtained per sample depends on the count rate and counting time of each isotope. On average the total counting time during one sample analysis is about 5 seconds per isotope. Assuming a concentration of 1 ppb in the sample, this will give a count rate of ~10 cps, although it might vary with sensitivity of the element and its isotopic abundance. During the 5 seconds counting time, this example would give 50 counts in total. In an ideal situation, the resulting standard deviation just from counting statistics should then be ± 7 counts (square root of 50), i.e. 14% relative standard deviation. To improve the precision (and therefore detection limits), longer counting times can be used, especially for important low level analytes (e.g. B and As) and isotopes with low abundances (e.g. Ca, Se, Cd).



Figure 4: Bricks of multicrystalline silicon base material for the production of solar cells.

Conclusion

The direct GD-MS analysis of crucial impurities in solar cell silicon (Mg, Al, Ca, Ti, V, Cr, Fe, Ni, Cu, As, Zr) show typical detection limits of 1 ppb in some cases but often very much lower. These detection limits were obtained with minimum sample preparation, primarily grinding and acid cleaning of the sample surface.

All concentrations measured are semiquantitative since Standard RSF's have been used. Nevertheless, the relative variations between samples will be accurate, therefore providing a valuable tool for production and contamination control in solar cell industry.

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Related Thermo Scientific Products for the Analysis of Silicon

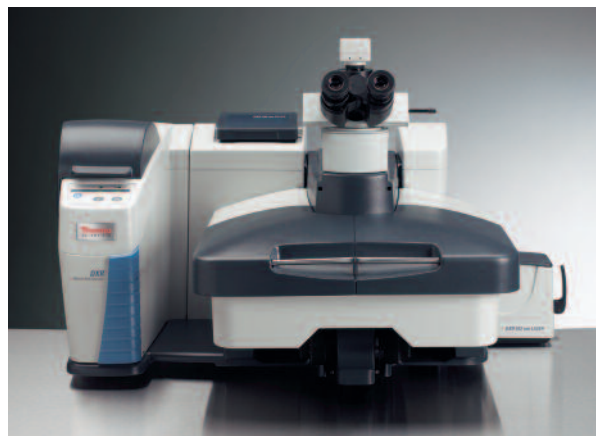
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