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Analysis of solar cell silicon

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Introduction
The 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™ Plus Glow Discharge Mass Spectrometer 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 Plus GD-MS 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 Plus GD-MS 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 consisted 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 were 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 were significantly reduced, therefore minimizing any analytical uncertainities 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:

- Grinding the Si sample into shape (at least one flat side, min. 20 mm, max. 60 mm diameter)
- Grinding the sample surface (using grid 220 followed by grid 600 diamond grinding discs; HD Piano, Struers GmbH, Germany)
- Washing the surface with DI (deionised) water
- Removal of contamination from surface with 10% ultrapure HNO_3
- Washing the surface with DI water
- Removal of the top surface layer with 20% ultrapure HF
- Washing the surface with DI water
- Rinsing with isopropanol
- Drying with Ar stream.

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:

Instrumental settings
Discharge current: 65 mA (continuous DC mode)
Discharge voltage: ~ 1000 V
Discharge gas: 400 ml Ar min^{-1}
Matrix sensitivity: 1 x 10^{10} 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 Anode Tube
- 2 Plug-in extraction lenses
- 2 Sapphire insulation rings
- 2 Holding rings for Plug-in cones
- 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 $^{28}Si^{36}Ar$ and $^{28}Si_2$ 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 1 and 2).

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.

Table 1. Major interferences.

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	$^{28}Si^{36}Ar$
^{65}Zn	$^{28}Si^{38}Ar$
^{65}Zn	$^{30}Si^{36}Ar$
^{68}Zn	$^{30}Si^{38}Ar$
^{68}Zn	$^{28}Si^{40}Ar$
^{74}Ge	$^{38}Ar^{36}Ar$

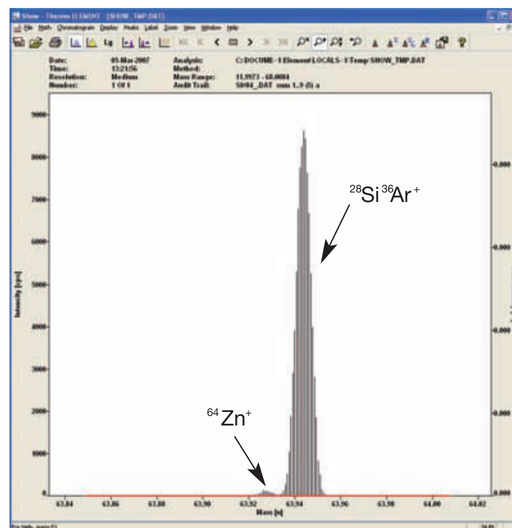

Figure 1. Medium resolution scan (R = 4000) of $^{64}Zn^{+}$ resolved from $^{28}Si^{36}Ar^{+}$.

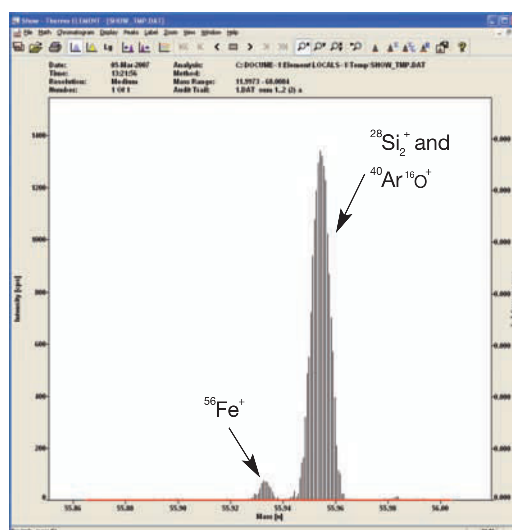

Figure 2. Medium resolution scan (R = 4000) of $^{56}Fe^{+}$ resolved from $^{28}Si_2^{+}$.

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.

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	< LoD	2.9
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	1.8	0.7
Ga	71	HR	< LoD	1.4
Ge	71	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	MR	< 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

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 Plus GD-MS' 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 x 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).

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.

Acknowledgements

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Related Thermo Scientific products for the analysis of silicon

Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer
Analysis of oxygen and carbon in solar silicon by the world leader in FT-IR. Wafer stage analysis of whole wafers or pieces. Complete suite of analytical software for both production and laboratory applications.

Figure 3. Bricks of multicrystalline silicon base material for the production of solar cells.

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DXR Raman microscope

Applications for solar cell development with Raman spectroscopy: Easily distinguish amorphous and crystalline silicon. Quantify percent amorphous and crystalline silicon. Map distribution of amorphous and crystalline silicon across a surface.

K-Alpha Photoelectron Spectrometer XPS Spectrometer

Precise chemical characterization of multilayered devices such as solar cells can be problematic. Careful control of the chemical composition for each layer is vital to the performance and efficiency of such devices. XPS can provide quantitative elemental and chemical characterisation of individual layers within the cell. Exploitation of the nm depth resolution of XPS allows chemical analysis of interface chemistries arising between the many layers.

Find out more at **thermofisher.com/GD-MS**

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