Challenges in GD-MS analysis of PV silicon materials

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Why do we need to measure impurities in PV silicon?

Raw Materials

Silicon value chain
Role of impurities in solar cell silicon

Quantitative measurements?

Photo: Melinda Gaal

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Why do we need to measure impurities in PV silicon?

$Istratov\ et\ al.,\ Mat\ Sc\ Eng\ B\ (2006)$

$10^{18}\ cm^{-3}$

$10^{16}\ cm^{-3}$

$10^{13}\ cm^{-3}$

$10^{13}\ cm^{-3}$

$10^{16}\ cm^{-3}$

$10^{18}\ cm^{-3}$

$Davis\ et\ al.\ (1980),\ IEEE\ Transactions$
Outline

- Trace element analysis in PV silicon
  - Occurrence in the matrix
  - Quantification of trace elements

- Applications of GD-MS for PV silicon:
  - Concentration of doping elements
  - Concentration of metal impurities

- Summary
Silicon for photovoltaics

- Si is a semiconductor material ⟷ the concentration of doping elements influences the possibility to perform GD-MS analyses

- Typical concentrations of doping elements (p-type solar cells) are in the range 110 – 300 ppba ⟷ resistivity in the range 1 – 2.5 Ω cm
Analytical methods for trace elements analysis in PV silicon

- Impurities are present in Si for photovoltaics in 2 states:
  - Dissolved into the Si matrix: O$_i$, C$_s$, Fe$_i$, …
  - As precipitates: metal-based, Si$_3$N$_4$, SiC …

- Impurities can be affected by macro- and micro-segregation $\Leftrightarrow$ different techniques are available / suitable to measure the impurities
Experimental setup

Flat samples - sample size:
max. Ø 70 mm, 40 mm height
min. Ø 20 mm

Analysed area: Ø ~ 8mm

Bulk measurement, average over a wide area

Sputtering rate = 20 nm/sec
Quantification of trace elements

The quantification of the concentration of the elements is done according to:

\[ C_X = \frac{I_X}{I_M} \cdot \frac{A_M}{A_X} \cdot \text{RSF} \]

- \( C_X \): concentration of element (isotope)
- \( C_M \): concentration of matrix (Si\(^{28}\))
- \( I_X \): intensity (cps) of element
- \( I_M \): intensity (cps) of matrix
- \( A_X \): abundance of element (isotope)
- \( A_M \): abundance of matrix (Si\(^{28}\))
- \( \text{RSF} \): relative sensitivity factor (element-specific)

Ion Beam Ratio (IBR) = \( \frac{I_X}{I_{Si}} \)

[Image: 'dirty' reference sample]
Applications of GD-MS for PV silicon materials

- Concentration of doping elements:
  - Indirect measurement of resistivity
  - Comparison with direct measurement of resistivity

- Concentration of metal impurities:
  - Important to understand their effect on the electronic properties of Si
Applications - Dopant concentration

mc-Si with Al doping, p-type semiconductor

\[ N_{\text{acceptor}} = \frac{c_1}{\rho} + \frac{c_2}{f(\rho)} \]

ASTM F723-99

\[ \text{Di Sabatino et al., EUPVSEC (2007)} \]
Applications - Dopant concentration from Fe-acceptor pairing

Minority carrier lifetime before and after light soaking (Fe-B pairs dissociate) → calculate B, N_A and P, N_D → comparison

B and P by GDMS

Macdonald et al., EUPVSEC (2008)
Applications - Net doping in compensated silicon

Compensation ⇔ high content of acceptor (B) and donor (P) species

conversion equation from ASTM F723-99 for p- or n- type may be applied to the net doping

developed method by GDMS

\[ N_{\text{NET}} = (B+Al) - (P) \]

Modanese et al., PiP (2011)
Applications - Fe addition

- 50 ppmw Fe were added to the Si melt
- Given the low segregation coefficient ($C_{\text{sol}} / C_{\text{liq}} \approx 10^{-5}$), most of the Fe segregates towards the top of the ingot (last to solidify) $\Rightarrow$ non-homogeneous distribution

Kvande et al., JAP (2008)
Applications - Study of grain boundaries

Metal impurities in PV Si can form precipitates:
- they are detrimental for electronic properties
- they usually segregate at grain boundaries

Selected areas:
- SG1: single grain, area 1
- GB1: (random) grain boundary, area 1
- TB1: twin boundary, area 1

Is there any difference due to sample microstructure (i.e. random grain boundary, single grain, twin boundary)?
Applications - Study of grain boundaries (continue)

Selected impurities in mc-Si: Fe and Cu

Selected areas:
- SG1: single grain, area 1
- GB1: (random) grain boundary, area 1
- TB1: twin boundary, area 1

➢ No clear evidence of precipitates ⇔ too low concentrations ?

No pre-sputtering!
Applications - Depth profiling and investigation of precipitates

- p-type Si ingot, with 50 ppmw \(1.25\times10^{18}\ \text{cm}^{-3}\) Fe and 128 ppbw \(1.66\times10^{16}\ \text{cm}^{-3}\) B added to the melt (prior to casting)

No pre-sputtering!
Applications - Depth profiling and investigation of precipitates

- Non-homogeneous Fe concentration
- Averaging over several repeated analyses
- Low Fe levels, although the impact on electronic properties is strong at these low concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si28 (cps)</th>
<th>Fe56 (ppbw)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVG</td>
<td>STDEV</td>
</tr>
<tr>
<td>85%</td>
<td>1.01x10^9</td>
<td>9.64x10^6</td>
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<td>88%</td>
<td>1.61x10^9</td>
<td>6.77x10^7</td>
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<td>90%</td>
<td>4.15x10^9</td>
<td>2.56x10^7</td>
</tr>
<tr>
<td>91%</td>
<td>2.69x10^9</td>
<td>5.13x10^7</td>
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<td>2.72x10^8</td>
</tr>
<tr>
<td>91%</td>
<td>5.51x10^9</td>
<td>6.48x10^7</td>
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</table>

- Homogeneous B concentration
- Compared to Fe, lower number of analyses required
- Important to have a precise quantification due to the B impact on the conductivity
Challenges in the study of GB and dislocations

Conclusion:
- 300 nm particle with 0.5% M $\Leftrightarrow$ 0.5x10$^{-9}$, below LoD!
- Estimation of the size of precipitates for detection $\Leftrightarrow$ to give 5 ppb M, a single particle should have $\varnothing = 660$ nm!
Concluding remarks

- GDMS can provide **reproducible** measurements of doping and trace elements in silicon for photovoltaics, with **precise quantification** down to **low-ppb** levels

- Applications for PV Si - examples:
  - Concentration of **doping elements**: doping, net doping
  - Concentration of **metallic impurities**: segregation profile, relation to micro- and macro-segregation

- Further work: tuning of measurements for precipitates analysis