Future Potential for SoG-Si Feedstock from Metallurgical Process Route

Kristian Peter, Radovan Kopecek
*International Solar Energy Research Center Konstanz, Germany*

Anne-Karin Soiland, Erik Enebak
*Elkem Solar AS, Kristiansand, Norway*
Contents

Introduction

Modeling: Si feedstock cost – cell efficiency – carrier lifetime

The importance of defect gettering and engineering

Lifetime monitoring over advanced cell process

Influence of compensation

Summary and conclusion
Introduction
Members, Sponsors:

Centrotherm
Rena
Sunways
Erso
AM (Baccini)
PV Cystalox
Elkem Solar
Semilab
Micron
Sefar
Polymer Kompositer
City Konstanz
Stadtwerke KN
Prof. E. Bucher
Alice Wartemann-Stiftung

Private research institute in Germany
Foundation: December 2005
Opening R&D: September 2007

International Solar Energy Research Center Konstanz
Elkem Solar’s Solar Grade Silicon Production Process

- **Metallurgical silicon**
  - In-house production only
  - Based on Elkem's core competencies

- **Slag treatment**
  - Three sequential purification steps designed to reduce the level of impurities for critical elements
  - Largely based on Elkem’s core competencies in high temperature processes, process and equipment design

- **Leaching**

- **Solidification**
  - Ingots cleaned and sawed into bricks of ~10 kg
  - Quality control

- **Post treatment**
Elkem Solar Silicon (ESS) vs poly silicon reference

\[ \eta [\%] \]

\begin{align*}
\text{Reference} & \quad 18.5 \\
65\% \text{ ESS} & \quad 18.5 \\
75\% \text{ ESS} & \quad 18.5 \\
100\% \text{ ESS} & \quad 18.5 \\
\end{align*}

-> V. Hoffmann et al: **2BO.3.3 Tuesday 17:00**
First Results on Industrialization of Elkem Solar Silicon at Q-Cells AG

<table>
<thead>
<tr>
<th>4 cm² lab-cells</th>
<th>( \eta [%] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FZ Reference</td>
<td>18.5</td>
</tr>
<tr>
<td>100% Elkem</td>
<td>18.5</td>
</tr>
<tr>
<td>100% Elk, LID FhG-ISE Cal lab</td>
<td>18.1</td>
</tr>
</tbody>
</table>

M. Käs et al.,
4th WCPEC, Hawaii 2006
Modeling:
- Silicon feedstock cost
- Solar cell efficiency
- Minority carrier lifetime
Examples of production cost for multicrystalline silicon solar cell modules
Examples of production cost for multicrystalline silicon solar cell modules
Indicative correlation between cell efficiency and minority carrier lifetime for standard and more advanced c-Si cell concepts (PC1D simulation)

**Question:** Do SoG-Si wafers from metallurgical refining process keep up with future cell concepts?
Indicative correlation between cell efficiency and minority carrier lifetime for standard and more advanced c-Si cell concepts (PC1D simulation)

**Question:** Do SoG-Si wafers from metallurgical refining process keep up with future cell concepts?
Indicative correlation between cell efficiency and minority carrier lifetime for standard and more advanced c-Si cell concepts (PC1D simulation)

**Question:** Do SoG-Si wafers from metallurgical refining process keep up with future cell concepts?
The importance of defect gettering and engineering
Mechanisms of impurity gettering

Impurities are collected at sites where the negative effects are minimized.

- **Atomic trapping at lattice defects**
- **Precipitation of metal-silicides** at the surface or at structural defects such as grain boundaries or dislocations
- **Interaction with electronic dopants** due to electrostatic attraction between ionized dopant atoms and oppositely charged metals
- **Segregation into a region very highly doped with phosphorus**, in which the impurity solubility is significantly higher
BUT:

In contrary, during high temperature processes, metallic precipitates may act as contamination sources and will reduce the material quality.
Defect engineering

Buonassisi et al. (University of California, Berkeley, now with MIT):

Size, spatial distribution, and chemical binding of metals within clusters is just as important as the total metal concentration in limiting the performance of multicrystalline silicon solar cells.

-> concept of defect engineering by optimizing growth and processing sequences to trap metals in their least harmful state.

S. Hudelson et al., 2DP.2.2 (Thursday 10:30)  
Mitigating the “Iron Problem” in Crystalline Silicon Solar Cells

M. Rinio et al., 1AO.2.1 (Monday)  
Defect Redistribution by 400 °C Anneal in Typical Ingot Silicon Solar Cells

Iron point defect reduction in multicrystalline silicon solar cells.  

Transition metal interaction and Ni-Fe-Cu-Si phases in silicon.  
Lifetime monitoring over an advanced cell process
1. Multicrystalline p-type Si wafer
2. 100 Ω/sq POCl₃ diffusion, 800°C
3. SiN deposition by LPCVD, 780°C
4. 10 Ω/sq POCl₃ diffusion, 950°C
5. Al screen printing and firing
6. μ-induced remote H-passivation
Measurement of minority carrier lifetime by μ-PCD mapping after each process step of an high efficiency cell process

1. 100% Elkem Solar wafers
2. 
3. B. Raabe PhD Thesis Univ. of Konstanz
4. 2CV.4.70
5. 
6. etch off and chemical passivation
initial wafer

Reference wafer  \( \mu \)-PCD map  Elkem SoG-Si wafer
shallow phosphorous diffusion (100 Ω/sq)
LPCVD SiN surface passivation

Reference wafer

μ-PCD map

Elkem SoG-Si wafer
strong phosphorous diffusion (10 $\Omega$/sq)

Reference wafer  $\mu$-PCD map  Elkem SoG-Si wafer
screen printing of aluminum and sintering

Reference wafer  μ-PCD map  Elkem SoG-Si wafer
microwave induced remote hydrogen passivation

Reference wafer

µ-PCD map

Elkem SoG-Si wafer
Comparison with different suppliers

Normalized effective lifetime for different suppliers to investigate high temperature POCl₃ diffusion stability
# Boron BSF: High temperature process on mc-Si Wafer

<table>
<thead>
<tr>
<th>mc-Si wafer</th>
<th>$j_{sc}$ [mA/cm$^2$]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elkem Solar</td>
<td>34,3</td>
<td>16,1</td>
</tr>
<tr>
<td>Reference</td>
<td>33,2</td>
<td>15,4</td>
</tr>
</tbody>
</table>

*Figures show the solar cell structure with layers such as Ag, ARC, n+, p, p+.*

- **Boron BSF solar cell**

<table>
<thead>
<tr>
<th>mc-Si wafer</th>
<th>$j_{sc}$ [mA/cm$^2$]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elkem Solar</td>
<td>26,9</td>
<td>12,4</td>
</tr>
<tr>
<td>Reference</td>
<td>21,7</td>
<td>9,9</td>
</tr>
</tbody>
</table>

A. Kränzl  
PhD Thesis  
Univ. of Konstanz
Influence of compensation
Compensation of p-type Si by phosphorous results in:

- reduction of carrier concentration
- shift of Fermi level
- change of occupation of defect levels
- increase in minority carrier lifetime
- increase of resistivity

Investigation of three different mc-Si wafers:

- Reference 1.5 Ωcm
- Elkem SoG-Si 1.4 Ωcm
- Elkem + B + P 1.7 Ωcm
Depth profiles measured by ECV (electrochemical capacity-voltage)
Mobility from carrier concentration and resistivity measurements

-> compensation reduces the majority carrier mobility
Mobility of majority carriers (holes)

Reduced mobility in compensated material measured by many other research groups, e.g:

J. Libal et al., 2DO.1.5 Thursday 13:30
Study of Compensation Effects in Cz-Silicon Grown from Solar Grade Silicon Feedstock

![Graph showing decreasing Hall mobility with increasing compensation](image)

Decreasing Hall-mobility with increasing compensation
Comparison of transport properties

<table>
<thead>
<tr>
<th>Na+Nd/Na-Nd</th>
<th>$\rho$ [10$^{16}$ cm$^{-3}$]</th>
<th>$\rho$ [Ωcm]</th>
<th>$\mu$ [cm$^2$/Vs]</th>
<th>Voc * [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>~ 1</td>
<td>1.4</td>
<td>1.5</td>
<td>304</td>
</tr>
<tr>
<td>Elkem</td>
<td>~ 2</td>
<td>1.9</td>
<td>1.4</td>
<td>242</td>
</tr>
<tr>
<td>Elkem + B + P</td>
<td>~ 3</td>
<td>1.8</td>
<td>1.7</td>
<td>207</td>
</tr>
</tbody>
</table>

* Average of 20 cells each, $\eta$=16,0%

For compensation, samples with same doping concentration $p$ should be compared rather than samples with same resistivity $\rho$

$p \rightarrow$ Voc, $j_{sc}$ ($\tau$)

$\rho \rightarrow$ $\rho_{\text{Series}}, \text{FF}$, can be engineered (distance between contact points…)

33
Light induced degradation in compensated Cz SoG-Si cells

R. Kopecek et al., 2DV.1.5
Crystalline Si Solar Cells from Compensated Material: Behaviour of Light Induced Degradation
Very high compensation: Na ~ Nd

Extremely high lifetimes of $\tau > 800 \mu s$ are measured in highly compensated wafers from the top region of the multicrystalline silicon ingot ($\rho > 10 \ \Omega cm$, still p-type).
Very high compensation: Na ~ Nd

See also:

D. Macdonald et al: 1BP.3.2 (after this presentation)
Carrier Lifetime Studies of Strongly Compensated p-type Czochralski Silicon

S. Dubois et al: 2CV.4.36
Beneficial Effects of Dopant Compensation on Carrier Lifetime in Metallurgical Grade Silicon
Compensation

The improvement of the minority carrier diffusion length in spite of the relatively high concentration of both B and P was reported by many authors. The effect was explained by:

- the Fermi level shift
- a hypothesis, that B-O defect formation occurring in B doped silicon is inhibited by B-P interaction.

Phosphorous seems to prevent boron from B-O complex formation!

References


Summary and conclusion
Summary

• High minority carrier lifetimes achievable in SoG-Si from metallurgical process route even after high temperature processes.

• Reduced majority carrier mobility in compensated material. Only minor influence on cell performance expected for adequate cell design.

• Compensation:
P-B interaction may compete with B-O recombination centers.

Thus moderately compensated Si may be applied for high η Si solar cells.
Conclusion

For Elkem Solar wafers it is likely that isolated precipitates may act as gettering centers for impurities originating from the crucible during multicrystalline ingot growth.

It is demonstrated that SoG Si feedstock from metallurgical process route may keep up with future advanced cell concepts such as
- selective emitters
- rear side passivated cells

Efficiencies of 18% and higher are feasible on thin multicrystalline wafers

Typical impurities levels produced through the Elkem Solar industrial demo plant:

- **Feedstock:**
  - Boron: 0.4 ppmw,
  - Phosp.: 1.5 ppmw
  - Metals: <30 ppmw

- **Wafer:**
  - $\rho = 0.8 \ \Omega cm$ (typical value)
  - Characteristics of a non-compensated 0.5 $\Omega cm$ material
Acknowledgements

Co-authors:  Radovan Kopecek, ISC Konstanz
            Anne-Karin Soiland, Elkem Solar
            Erik Enebakk, Elkem Solar

PhD Students:  Bernd Raabe, Martin Käs, Andreas Kränzl

R&D groups:  ISC Konstanz and Elkem Solar
Solar electricity and light for poor people in Cameroon

Solar cells from our research are donated to Cameroon to improve the living conditions in villages, schools and hospitals.