Thermodynamics on SOG-Si Refining Processes

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Recent Research Fields

- Physical Chemistry of High Temperature Processing (Steelmaking and Waste Management)
- Microwave Processing for Recycling and Waste Treatment
- Thermodynamics and Processing on Solar Grade Silicon (SOG-Si) Production
Contents

1. Introduction

2. Metallurgical refining for SOG-Si
   - Thermodynamic properties of impurities in molten Si alloys -
   - Optimized Process Combined with Leaching Treatment -

3. Solidification refining of Si with Si-Al melts
   - Segregation ratios of impurities between solid Si and Si-Al melt -

4. Conclusions and Future Work
Requirement for metallurgical refining process for SOG-Si

Depending on off-grade Si for semiconductor

Increase in solar cell production

Fig. Amount of solar cell production by various processes.
Possibility of Low Cost SOG-Si Production

Can we remove impurities from MG-silicon by metallurgical refining processes?

New Refining Process?
Impurities and solar cell efficiency

Fe, Ti, Al, P, B

Table 1  Impurity contents in MG-Si.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Content(ppma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1300</td>
</tr>
<tr>
<td>Ti</td>
<td>220</td>
</tr>
<tr>
<td>Al</td>
<td>3300</td>
</tr>
<tr>
<td>P</td>
<td>30</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
</tr>
</tbody>
</table>

Fig. Solar-cell efficiency versus impurity concentration for 4-\(\Omega\)•cm p-base devices.
Strong Affinity of Silicon for Oxygen

Difficulty in Oxidation Treatment

Fig. Ellingham diagram for some representative elements.
Most metallic impurities

P, B, C, etc.

Fig. Relationship between Gibbs free energy and phase diagram below melting point of silicon.

(a) Small segregation coefficient

(b) Large segregation coefficient
Fig. Removal of impurity in silicon by solidification refining.
Thermodynamic properties of impurities in molten silicon alloys

- **Phosphorous**
  Equilibrated in a controlled phosphorous partial pressure

- **Titanium and Iron**
  Equilibrated with lead

- **Aluminum, Calcium and Magnesium**
  Equilibrated with Oxides
Thermodynamics of P in Molten Silicon

Fig. Schematic Cross Section of Experimental Apparatus.

1. Gas Inlet Tube
2. Mullite Tube
3. Graphite Holder
4. Graphite or Alumina Crucible
5. Molten Si-P Alloy
6. Porous Alumina Block

Fig. Schematic cross section of the phosphorus vapor generator.

Red Phosphorus Temperature 398-461K
Argon Flow Rate 190cc/min

To Ribbon Heater
Temperature Controller
Thermocouple
Silicone Plug

Red Phosphorus
Ribbon Heater

Argon Flow Rate 190cc/min
$1/2 \text{P}_2(\text{g}) = \text{P(}\text{mass\%}, \text{ in Si})$

$\Delta G^\circ = -139,000 + 43.4T \text{ (J/mol)}$

Fig. Relationship between equilibrium phosphorous partial pressure and phosphorous concentration of silicon at 1823K.

Fig. Temperature dependence of free energy change of phosphorous dissolution into silicon.
Fig. Relationship between equilibrium partial pressure of P, P$_2$ and phosphorous content of silicon at 1823K.

Hertz-Knudsen equation

\[
\frac{dy}{dt} = \sqrt{\frac{M_i}{2\pi RT}} \cdot \gamma_i \cdot p_i^0 \cdot X_i
\]

Ikeda et al.

1823K 1867K

estimated estimated

Suzuki et al. Yuge et al.

Fig. Relationship between time for vacuum treatment and (V/A) • log([mass%P]/[mass%P]$_0$).

Ikeda et al.
Thermodynamics of Ti and Fe in Molten Silicon

Fig. Schematic Cross Section of Experimental Apparatus.

Gas Inlet Tube
Mullite Tube
Graphite Holder
Graphite Lid
Graphite Crucible
Molten Si-M
(M:Fe,Ti)
Molten Lead
Porous Alumina
Block

Fig. Phase diagram of Si-Pb system.
Fig. Relationship between $X_{\text{Ti in Si}}$ and $\ln X_{\text{Pb in Pb}} - \ln X_{\text{Pb in Si}}$ at 1723K.

Fig. Relationship between $X_{\text{Fe in Si}}$ and $\ln X_{\text{Pb in Pb}} - \ln X_{\text{Pb in Si}}$ at 1723K.
Ti and Fe are stable in molten silicon. Removal of Ti and Fe by chemical reaction (i.e. oxidation, chlorination) is considered to be impossible. Double solidification process is required.
Thermodynamics of Al, Ca and Mg in Molten Silicon

Fig. Schematic Cross Section of Experimental Apparatus.
Fig. Temperature dependence of the activity coefficient of aluminum, calcium, and magnesium in molten silicon relative to pure liquid.

\[
\ln \gamma_{\text{Al}} = -\frac{3610}{T} + 0.452 \\
\ln \gamma_{\text{Ca}} = -\frac{14300}{T} + 1.55 \\
\ln \gamma_{\text{Mg}} = -\frac{11300}{T} + 4.51
\]
P, Al, Ca and Mg can be removed by vacuum melting.

mass of Si : 1000kg
surface area  --- 40.3m²  ---- 0.739m²

mass ppm P
mass ppm Al, mass ppm Ca

Fig. Relationship between vacuum time and impurity content of silicon at 1823K.
NEDO SOG-Si Manufacturing Process (Operated in JFE Steel Co.)

Lower cost refining process is desired to be developed.
Is there any way to reduce the times of solidification refining?

If the treatment of MG-Si can remove 90% of Ti and Fe, ..... 

Possibility of Acid Leaching
Si-Ca-Fe or Ti dissolved at 1723K

Cooling to 1300K (CaSi$_2$ formation)

Acid leaching with aqua regia

Chemical analysis
Removal Fraction of Fe

Fig.: Relationship between cooling rate of molten silicon and removal ratio of Fe after acid leaching.
Consideration of Removal Behavior of Fe with the Ca-Fe-Si Phase Diagram

Fig. Phase Diagram of the Si rich corner for the Ca-Fe-Si System [calculated by Thermo-Calc]

Eutectic Point
\[ \frac{X_{Ca}}{X_{Fe}} \equiv 6.4 \]

Secondary Phase
CaSi₂ or FeSi₂ ?
Si-3.26%Ca-0.424%Fe, 4.4K/min

Fig.
(a) SEM micrograph of Si-Ca-Fe alloy.
(b) Microstructure of Si-Ca-Fe alloy.
(c) Concentration profile by EPMA line analysis.
Si-2.41%Ca-0.685%Fe, 4.4K/min

Fig.
(a) SEM micrograph of Si-Ca-Fe alloy.
(b) Microstructure of Si-Ca-Fe alloy.
(c) Concentration profile by EPMA line analysis.
Vacuum melting by electron beam

Plasma melting with water vapor

Directional solidification

SOG-Si

First step purification

Second step purification

MG-Si

Vacuum

Argon

Acid leaching treatment with Ca addition

Removal of Fe and Ti

Removal of P, (Al, Ca)
P : 30 → < 0.1 ppmw

Removal of B, C, (Al, Ca)
B : 5-10 → 0.1-0.3 ppmw

Removal of Fe, Ti, Al
Acid leaching treatment with Ca addition

Removal of Fe, Ti, P and B

First step purification
- Vacuum melting by electron beam
- Removal of P, (Al, Ca)
  \[ P : 30 \rightarrow < 0.1 \text{ppmw} \]

Second step purification
- Plasma melting with water vapor
- Removal of B, C, (Al, Ca)
  \[ B : 5-10 \rightarrow 0.1-0.3 \text{ppmw} \]
- Directional solidification
- Removal of Fe, Ti, Al
- Argon

MG-Si

SOG-Si

Reduction of processing time

NEDO SOG-Si Manufacturing Process
(Operated in JFE Steel Co.)

P : 30 \rightarrow < 0.1 \text{ppmw}

B : 5-10 \rightarrow 0.1-0.3 \text{ppmw}
Solidification refining of Si with Si-Al melt at low temperature.

**Low eutectic temperature**

**Removal of impurities by use of enhanced segregation at low temperature**

**Fig. Phase diagram of Si-Al system.**

**Segregation ratio**

\[
k_i = \frac{X_i \text{ in solid Si}}{X_i \text{ in Si-Al melt}}
\]

**MG-Si (98-99%)**

**Pure Al**
Segregation ratios of impurities between solid Si and Si-Al melt

- Thermodynamics of impurity elements in solid Si
  - Evaluation of low temperature Si refining process

Segregation ratios of impurities between Si-Al melt and solid Si

Al, B, P  ➔  Experimentally determined

Fe, Ti, etc.  ➔  Theoretically determined
Determination for segregation ratios of P and B

Diffusion coefficient of impurity elements in solid Si

Al, P, B … Considerably small diffusion coefficient in solid Si

Solidification method to attain the equilibrium

Fig. Diffusion coefficient of impurity elements in solid silicon.
Temperature Gradient Zone Melting (TGZM) method

Fig. Schematic diagrams of the temperature gradient zone melting.
(a) Portion of phase diagram. (b) Temperature gradient in system. (c) Physical system comprising (A+B)molten zone traveling through solid A.

Determination for segregation ratios of P and B

Solid Si
Precipitated Si
Si-Al melt

Components A and B

Distance

Temperature

L
L+S
C\textsuperscript{l}\textsubscript{1} C\textsuperscript{l}\textsubscript{2} C\textsuperscript{s}\textsubscript{1} C\textsuperscript{s}\textsubscript{2}
Determination for segregation ratios of P and B

Experimental method

*Temperature Gradient Zone Melting Method*

Al and P contents in solid silicon - Ar atmosphere 24-72h
EPMA analysis Temperature Gradient 10-40K/cm

Fig. 1. Schematic diagram of an experimental apparatus: 1-SiC heating element; 2-thermocouple connected to PID controller; 3-gas outlet tube; 4-stainless steel holder; 5-single crystalline silicon; 6-aluminum foil; 7-mullite tube; 8-thermocouple for measuring temperature of molten zone; 9-porous alumina boat 10-gas inlet tube; 11-alumina plate; 12-Sponge titanium

Distribution of P (and Al) between solid Si and Si-Al-P alloy
- Red phosphorus stuck Al foil

Distribution of B (and Al) between solid Si and Si-Al-B alloy
- Prepared Al-B foil
Sample after TGZM experiment

Fig. Photo of a TGZM specimen after the experiment.

Fig. Intensity profiles of $K_{\alpha}$ radiation of aluminum and phosphorus of the sample (accelerating voltage of 15kV, sample current of 200nA, sampling step of 10μm).
Segregation ratios of P and B

Segregation ratios are smaller at low temperature.

→ Low temperature refining is effective.
Derivation of segregation ratio of impurity elements between solid Si and Si-Al melt

Equality in chemical potential of impurity between solid Si and Si-Al melt

\[ G_{i}^{l0} + RT \ln a_{i}^{l} = G_{i}^{s0} + RT \ln a_{i}^{s} \quad 1) \]

\[ \ln k_{i} = \ln \frac{X_{i}^{s}}{X_{i}^{l}} = \frac{\Delta G_{i}^{\text{fus}}}{RT} + \ln \frac{\gamma_{i}^{l0}}{\gamma_{i}^{s0}} \quad 2) \]

Activity coefficients in solid Si and Si-Al melt

\[ \text{Based on the reported thermodynamic data} \]
### Segregation ratios between solid Si and Si-Al melt

< Segregation coefficients between solid/liquid Si

<table>
<thead>
<tr>
<th>Element</th>
<th>Segregation ratio between Si-Al melt and solid Si</th>
<th>Segregation coefficient between solid/liquid Si at m.p. of Si$^{(6, 2)}$</th>
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<tbody>
<tr>
<td></td>
<td>1073K</td>
<td>1273K</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7×10^{-11}</td>
<td>5.9×10^{-9}</td>
</tr>
<tr>
<td>Ti</td>
<td>3.8×10^{-9}</td>
<td>1.6×10^{-7}</td>
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<tr>
<td>Cr</td>
<td>4.9×10^{-10}</td>
<td>2.5×10^{-8}</td>
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<td>Mn</td>
<td>3.4×10^{-10}</td>
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<tr>
<td>Ni</td>
<td>1.3×10^{-9}</td>
<td>1.6×10^{-7}</td>
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<td>Cu</td>
<td>9.2×10^{-8}</td>
<td>4.4×10^{-6}</td>
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<td>Zn</td>
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<td>1.7×10^{-6}</td>
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<td>In</td>
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<td>Sb</td>
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<td>Pb</td>
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<td>P</td>
<td>4.0×10^{-2}</td>
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<td>B</td>
<td>7.6×10^{-2}</td>
<td>2.2×10^{-1}</td>
</tr>
<tr>
<td>Al</td>
<td>1.4×10^{-4}</td>
<td>4.9×10^{-4}</td>
</tr>
</tbody>
</table>
Impurity contents of Si after low temperature solidification refining with Si-Al melt at 1273K and ordinary Si solidification refining of MG-Si.

Contents after purification; \( C_i = k_i C_i^{ini} \) ← Initial content (MG-Si)

- Contents of MG-Si
- Allowable contents for SOG-S Si
- Contents after solidification refining with Si-Al melt at 1273K
- Contents after ordinary solidification refining
Viewing the development of the solidification refining of Si with Si-Al melt at low temperature

- Discussion of the Si solidification method from Si-Al melt
- Refining test

Fig. Phase diagram of Si-Al system.
Discussion for separating of solid Si from Si-Al melt by flotation

\( \rho_{\text{solid Si}} < 2.33 \text{g/cm}^3, \rho_{\text{Al-25.8\%Si}} \sim 2.45 \text{g/cm}^3 \)

Holding Si-55.3at\%Al alloy (liquidus temp. 1273K) at 1173K for 12h
Si saturated, solid fraction = 0.168

*Needle like Si grains*

Preparation – Melting in the induction furnace and rapid cooling
Separation of solidified Si from Si-Al melt using electromagnetic force — Induction furnace

Si-55.3at%Al alloy (liquidus, 1273K) was melted and held at 1323K in the induction furnace

Measuring the surface temp. of the melt by the infrared pyrometer

Cooling and Solidifying the sample by lowering from the position of induction coil
Solidified Si-Al alloy using induction furnace

Agglomeration of solidified Si by electromagnetic stirring
Agglomeration mechanism of Si under the fixed alternative magnetic field

- Difference in induced swirl current to the perpendicular direction
- Solidification of Si at lower position
- Downward bulk flow

Agglomeration of Si grains to the bottom of the sample

→ Solidification refining test
Experimental method

Fig. Schematic cross section of experimental apparatus.

Crashing the Si agglomerated part (> 840 μm), then acid cleaning

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrSi-1</td>
<td>4500</td>
<td>691</td>
<td>1280</td>
<td>56</td>
<td>36</td>
</tr>
<tr>
<td>PrSi-2</td>
<td>2160</td>
<td>248</td>
<td>1560</td>
<td>36</td>
<td>19</td>
</tr>
</tbody>
</table>
### Impurity contents of refined Si in the test run (ppmw)

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Source</th>
<th>Fe</th>
<th>Ti</th>
<th>B</th>
<th>P</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR-1</td>
<td>PrSi-1</td>
<td>13</td>
<td>(99.7%)</td>
<td>5.2</td>
<td>(99.2%)</td>
<td>0.81</td>
</tr>
<tr>
<td>SR-2</td>
<td>PrSi-1</td>
<td>13</td>
<td>(99.7%)</td>
<td>2.7</td>
<td>(99.6%)</td>
<td>0.88</td>
</tr>
<tr>
<td>SR-3</td>
<td>PrSi-2</td>
<td>20</td>
<td>(99.1%)</td>
<td>2.8</td>
<td>(98.9%)</td>
<td>0.71</td>
</tr>
<tr>
<td>SR-4</td>
<td>PrSi-2</td>
<td>27</td>
<td>(98.8%)</td>
<td>4.5</td>
<td>(98.2%)</td>
<td>1.90</td>
</tr>
<tr>
<td>SR-5</td>
<td>PrSi-1</td>
<td>47</td>
<td>(99.0%)</td>
<td>7.7</td>
<td>(98.9%)</td>
<td>0.98</td>
</tr>
<tr>
<td>SR-6</td>
<td>PrSi-1</td>
<td>36</td>
<td>(99.2%)</td>
<td>5.6</td>
<td>(99.2%)</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fe, Ti... Well reduced but not as well as predicted values
B, P... Effectively removed

High ability for purification was confirmed.
Proposal of refining process for SOG-Si

- Reduction of SiO₂ in arc furnace
- Alloying of silicon with Al
- Solidification refining with Si-Al melts
- Acid cleaning
- Pre-refined Si (5N except Al)
- Vacuum melting by electron beam
- Removal of P, (Al, Ca)
- Directional solidification
- Removal of Fe, Ti, Al
- SOG-Si
Conclusions and Future Work

The optimum metallurgical refining process for SOG-Si was thermodynamically assessed.

Possibility of solidification refining of Si with Si-Al melt was clarified. Solidification and separation of Si from the melt is the major problem to solve for the practical process.
Acknowledgments

Present data are based on two Doctoral Dissertations by Takahiro Miki (1999), now a research associate of Tohoku University, and Takeshi Yoshikawa (2005), now an assistant professor of Osaka University.
Periodical Journal Publication List 1

Metallurgical Refining

Solidification Refining