Background
Supply of SOG-Si

Fig. Amount of solar cell production in the world.

Depending on off-grade Si for semiconductor.

Short supply of Si for solar cell.
Metallurgical process
(NEDO SOG-Si manufacturing process)

First step

Vacuum melting (Removal of P)

Directional solidification
Removal of Fe, Ti, Al

Second step

Plasma melting with water vapor (Removal of B, C)

Directional solidification
Removal of Fe, Ti, Al

Difficulty in removal of P, B

Complicated process

High initial contents of Fe, Ti, Al

Necessity of multiple solidifications

Keeping at high temperature for a long time.

Much low cost process.
Solid solubilities of impurities in silicon
(After Trumbore)

Fig. Solid solubilities of impurity elements in Si.

Impurities are unstable at low temperature.

Possibility of Si refining at low temperature.
Phase diagram for the Si-Al binary system

Fig. Phase diagram of Si-Al binary system.

Solidification at low temperature.

Using metal solvent.

Enhanced segregation with Si-Al melt at low temperature.

Solidification refining of Si with Si-Al melt at low temperature.
Segregation coefficient of impurities between solid Si and Si-Al melt (After Yoshikawa)

Segregation coefficient \( k_i = \frac{X_i^S}{X_i^L} \)

Thermodynamic calculation.

Decrease of \( k_i \) at low temperature.

Effective solidification refining with Si-Al melt.

High purification ability of solidification with Si-Al melt.

Small segregation coefficient of P, B.

Fig. Segregation coefficient of P, B between Si and Si-Al melt.
Directional solidification of Si-Al alloy (After Yoshikawa)

**Fig.** Cross section of Si-Al alloy after directional solidification.

**Temperature gradient** 0.5 K/mm 5 K/mm

**Difficulty of bulk Si crystal growth.**

**Acid leaching to collect refined Si.**

**Table.** Impurity contents of Si (ppmw):

<table>
<thead>
<tr>
<th></th>
<th>MG-Si</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4500</td>
<td>691</td>
<td>56</td>
<td>36</td>
<td>1280</td>
<td></td>
</tr>
<tr>
<td>Refined Si</td>
<td>13(99.7%)</td>
<td>5.2(99.2%)</td>
<td>0.81(98.6%)</td>
<td>0.93(97.4%)</td>
<td>599(53.1%)</td>
<td></td>
</tr>
</tbody>
</table>

Lager than solid solubility. Contamination of melt?
Objective of this work

- Si crystal growth from Si-Al melt to prevent melt contamination.
- Investigation of the growth condition of bulk Si crystal from Si-Al melt.

- Directional solidification
  - Cooling rate
  - Temperature gradient
  - Classification of interface
  - Growth rate
Experimental procedure
Experimental procedure

Fig. Experimental apparatus.

Weighing (MG-Si, Al) ($X_{Si} = 0.447$, Liquidus temperature: 1273K)

Pre-melting (Induction furnace)

Ar purging

Melting (1323K, 30min.)

Directional solidification
Temperature gradient: 1.5 – 4.0 K/mm
Lowering rate: 0.02 – 0.08 mm/min

Observation
Experimental procedure

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

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Solid phase ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273 K</td>
<td>1173 K</td>
</tr>
<tr>
<td>0.139</td>
<td>0.447</td>
</tr>
</tbody>
</table>

Si growth will start at 1273K.

**Fig.** Schematic description of the experiment.
Results and Discussion
Si growth from Si-Al melt

Temperature gradient : 1.5 K/mm  Cooling rate : 0.062 K/min

Bulk Si crystal can be obtained from Si-Al melt.
Effect of cooling rate and temperature gradient

Temperature gradient 1.5 K/mm

Cooling rate (K/min)

0.12
0.105
0.084
0.062
0.031

Temperature gradient 4.0 K/mm

0.32
0.273
0.195
0.16
0.080
Classification of Si crystal / Si-Al melt interface

Rough

In-between

Flat

Pile up

200 μm

Al-Si eutectic

Si

20 μm
Growth rate of Si crystals and temperature gradient

Cooling rate
0.062 K/min

Temperature gradient
1.5K/mm

Length of Si crystal
3.1 mm

Experimental time
1925 min

Growth rate
1.6 x 10^{-3} mm/min

Growth rate (mm/min) = \frac{\text{Length of Si crystal (mm)}}{\text{Time (min)}}

Fig. Relationship between temperature gradient, Si growth rate and interface types.
Estimation of Si growth rate under diffusion control condition

Diffusion control condition

\[ V = D_{\text{Si in Si-Al melt}} \frac{\partial X_{\text{Si in Si-Al melt}}}{\partial x} \]
\[ = D_{\text{Si in Si-Al melt}} \frac{\partial X_{\text{Si in Si-Al melt}}}{\partial T} \cdot \frac{\partial T}{\partial x} \]

Temperature gradient

1. Inverse of liquidus slope
Estimation of Si growth rate under diffusion control condition

Good agreement with experimental results.

Si growth under diffusion control condition.

Fig. Relationship between temperature gradient, Si growth rate and interface types.
Impurity contents in refined Si

Table  Impurity contents in Si (ppmw) and removal fraction.
       (ICP atomic emission spectroscopy)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Al</th>
<th>Ti</th>
<th>B</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG-1</td>
<td>6040</td>
<td>1950</td>
<td>896</td>
<td>59</td>
<td>-</td>
</tr>
<tr>
<td>MG-2</td>
<td>1500</td>
<td>523</td>
<td>414</td>
<td>70</td>
<td>178</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>Fe (ppmw)</th>
<th>Al (ppmw)</th>
<th>Ti (ppmw)</th>
<th>B (ppmw)</th>
<th>P (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-1</td>
<td>MG-1</td>
<td>31.8(99.5%)</td>
<td>232(88.1%)</td>
<td>1.7(99.8%)</td>
<td>6.9(88.3%)</td>
<td>-</td>
</tr>
<tr>
<td>Re-2</td>
<td>MG-2</td>
<td>17.3(98.8%)</td>
<td>427(18.3%)</td>
<td>1.3(99.7%)</td>
<td>7.3(89.6%)</td>
<td>16(91.0%)</td>
</tr>
</tbody>
</table>

Solid solubility of Al: 1173K 160ppmw, 1273K 260ppmw

Melt contamination was prevented. High removal ratio could be obtained.
Conclusion

- Bulk Si crystal could be obtained from directional solidification of Si-Al melt with very low cooling rate.
- Growth rate of Si crystal, which has flat Si crystal / Si-Al melt interface, is controlled by diffusion of Si in the melt.
- Al content in refined Si was about solid solubility and other impurity elements can be removed efficiently.
Thank you for your kind attention.