Measurements and Analysis of Molten Silicon Temperature and Flow in Solidification Process of Solar Silicon

Seiko NARA¹, Toshio ISHII¹, Hirofumi MIYAHARA², and Keisuke OGI²

¹ Numerical Simulation Dept., JFE R&D Corporation, Kawasaki 210-0855, Japan
² Dept. of Materials Science & Engineering, Kyushu University, Fukuoka 819-0395, Japan

Abstract
In order to improve the conversion efficiency (up to a final target over 20% of conversion efficiency) of the photovoltaic cell with multi-crystalline silicon, it is necessary to optimize the casting conditions of silicon ingot such as purifications of mold, mold coating material, atmosphere gas and solidification rate. We have investigated the influence of solidification conditions on the microstructure by the experimental measurement of molten silicon temperature and the simulation of molten silicon flow and temperature distribution in rectangular crucible. It was detected that large supercooling in crucible bottom was effective in enlarging the crystal grain size. High quality silicon ingot was obtained by controlling the solidification rate.

The diffusion length of the wafer (thickness 5mm, resistivity 0.65Ω·cm, at bare state) was attained to 350μm or longer from this silicon ingot. Consequently, the conversion efficiency of the cell reached to 18.3% (cell area 25cm²) and 20.3%(cell area 4cm²) using this silicon wafer.

Key words
Molten Silicon, Flow, Temperature, Silicon Ingot, Diffusion Length, Simulation, Solar, Photovoltaic

1. Introduction
In the improvement in conversion efficiency of the photovoltaic system using multi-crystalline silicon, the quality of silicon wafers [1-5] is very important. To improve the quality of wafers [6-7], various methods (purification of the atmosphere, mold and coating materials, regulation of heating and cooling for large grain) have been carried out. The large grain was so effective for the conversion efficiency [5]. The grain size is generally affected by solidification rate. It is reported that the large grain grows under the solidification rate of 5[μm/sec] in small-size unidirectional experimental apparatus [8].

Therefore, in the present study, the experiment and simulation were carried out in several heat flux conditions for cooling under such the solidification rate. The molten silicon flow and temperature distribution were analyzed by the numerical simulation, and compared with the experimental results. Then, the large grain silicon ingots were produced by the regulation of solidification rate. The quality of silicon ingots was evaluated by measuring the diffusion length and conversion efficiency.

2. Simulation and Experiment
2.1 Mathematical modeling
The temperature of molten silicon flow in the crucible was analyzed using the solidification regulation method for the enlargement of silicon grain size. The molten silicon temperature is, generally, influenced by both of the thermal conductivity and the convection. Therefore, to estimate the molten silicon temperature, the fundamental equations were used as follows, where equation (1) is momentum equation, eq.(2) is continuity equation, and eq.(3) is energy equation.

\[ \rho \nabla \cdot \mathbf{v} = 0 \]  
(2)

\[ \nabla \cdot \left( \rho \mathbf{v} \right) = 0 \]  
(3)

The molten silicon was assumed to be incompressible fluid, and the change of density was small at the small incidence of temperature. So, boussinesq approximation was used in this simulation.

\[ \beta(T) = \beta(T_m) - \beta_0 (T - T_m) \]  
(4)

The calculation cell of the molten silicon in the crucible was shown in Fig. 1. The sidewalls in the crucible were assumed to be given constant temperature as equal to the furnace temperature. Heat flux was controlled at the bottom surface in the crucible according to the cooling condition. The center of the crucible was symmetry of the heat flow and the convective flow. Top of the specimen was considered thermal insulation and the slip surface. The RNG κ-ε method was used as solution method. As the calculation solver, FLUENT which was general flow analysis software was used.

![Fig. 1 Mesh of calculation area](image-url)
The initial and boundary condition were indicated in Table 1. The several different heat fluxes were applied at bottom in the crucible to compare the cooling states. The largest heat flux corresponded to the rapid solidification at the bottom surface. On the contrary, the smallest heat flux corresponded to slow solidification. To compare the temperature distributions on respective heat fluxes, the growth direction of the solidification was inferred. In addition, viscosity $\mu$, specific heat $c_p$, thermal conductivity $\lambda$, was assumed to be constant including supercooling range.

<table>
<thead>
<tr>
<th>Table 1 Initial and boundary condition</th>
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<tbody>
<tr>
<td>Structure of mesh</td>
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<tr>
<td>Initial condition</td>
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<tr>
<td>Boundary condition</td>
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<tr>
<td>Longitudinal wall</td>
</tr>
<tr>
<td>Top surface</td>
</tr>
<tr>
<td>Bottom plane</td>
</tr>
<tr>
<td>Slow solidification</td>
</tr>
<tr>
<td>Intermediate solidification</td>
</tr>
<tr>
<td>Intermediate solidification</td>
</tr>
<tr>
<td>Rapid solidification</td>
</tr>
<tr>
<td>Symmetric plane</td>
</tr>
</tbody>
</table>

2.2 Experimental procedure

The casting method in this experiment was used as the manufactured method for multi-crystalline silicon. The schematic figure of experimental equipment was shown in Fig. 2. The temperatures of the molten silicon and an atmosphere in this furnace were measured by the thermocouple (B-type) in the Alumina tube. Solidification rate was calculated from the movement of the position of solid-liquid interface measured by this Alumina tube or a silica rod. The heat flux was calculated from the temperature profile of the thermocouple in the chiller. The crystal growth of molten silicon in the furnace was recorded with a video recorder.

The experimental condition was shown in Table 2. Since the wafers made form the ingots is necessary the suitable resistivity (target resistivity: 0.5-5.0 $\Omega$cm) to make cells, the boron was doped in the silicon ingots. After manufacturing the silicon ingots, the wafer and cell were prepared and the physical and photovoltaic property was evaluated.

<table>
<thead>
<tr>
<th>Table 2 Experimental condition</th>
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<tbody>
<tr>
<td>Ingot seize</td>
</tr>
<tr>
<td>Silicon source</td>
</tr>
<tr>
<td>Target resistivity</td>
</tr>
<tr>
<td>Solidification rate</td>
</tr>
<tr>
<td>Atmosphere gas</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Results of simulation

The temperature of molten silicon in quarter part of crucible was shown in Fig. 3 as an example. As compared with the temperature near by the wall, the temperature of the center is lower. The tendency of temperature distribution was same in other calculations. Furthermore, the temperature at center bottom was lower than one of wall bottom. This tendency was correspondingly indicated in any calculations. Therefore, the position of the lowest and the highest temperature were the center bottom and the top corner, respectively.

![Temperature distribution in crucible](image)

The temperature along the longitudinal direction at center bottom was shown in Fig. 4. The temperature distribution tendencies of the respective heat fluxes were indicated almost same pattern. However, there were differences between the temperatures (supercooling) on the bottom with respective thermal conditions. The temperature on large heat flux (described as rapid solidification on table 1) was very low, that maend the large supercooling. On the contrary, the small heat flux (slow solidification on table 1) indicated small supercooling.
3.2 Experimental results

The molten silicon temperature distribution in the experiment was measured for ascertaining to correspond to the temperature distribution obtained by the simulation, where the heat flux was given for cooling condition. The results of the comparison the temperature of experiment and simulation were shown in Fig. 6. The heat flux for the cooling in the experiment was set to aim the rapid solidification. The temperature distribution indicated similar tendency on both experiment and simulation result. In addition, other experiments of silicon ingot production for silicon wafers were executed for avoiding the degradation of electrical property, which may be caused from contamination of impurities by the temperature measuring.

![Fig. 6 Molten silicon temperature of experimental and simulation at crucible center](image)

The comparison of crystal grain between the rapid solidification specimen and slow solidification specimen was shown Fig. 7. Fig. 7 indicated the distribution of the grain size and the number of grains along ingot height. The average grain size at Fig. 7 (a) was 25 [mm] at 5 [mm] height from the bottom. The one of Fig. 7 (b) was 7 [mm] at same height. This result revealed the ingot of larger grain size was made with rapid solidification condition at large heat flux at the bottom surface. It was presumed that the silicon grains at the bottom of the furnaces were apt to grow in the horizontal direction since the temperature gradient at the high heat flux was larger than that at the low heat flux in the vertical direction. The study about this phenomenon is continuously proceeded with.
Fig. 7 Distribution of number of grains and grain size in ingot height direction in rapid solidification process (a) and slow solidification ingot (b).

The diffusion length as an electric property was measured on the sliced wafers (5mm thickness, at bare state) from solidified ingots. The comparison of the diffusion length between rapid solidification specimen and slow solidification specimen was shown in Fig. 8. The diffusion length on the wafer, which sliced from the top of slow solidification ingot, was under 250μm as shown in Fig. 8 (b) and this value is insufficient for the photovoltaic property. On the other hand, the diffusion length at rapid solidification specimen exceeds 350μm and it was very high as shown in Fig. 8 (a).

Fig. 8 Mappings of distribution length at rapid solidification (a) and slow solidification (b) with resistivity at 0.65 Ω·cm

To compare electrical property between this rapid solidification ingot and the common single crystal wafer, the silicon ingots with rapid solidification condition were made in the range of resistivity from 0.5Ω·cm to 5Ω·cm. The comparison of average lifetime was shown in Fig. 9. Nevertheless this work’s wafers were sliced from multi-crystalline silicon ingot, the lifetime of this work’s silicon wafers indicated similar value of the lifetime on single crystalline silicon wafers [9].

Fig. 9 Correlation between resistivity and lifetime

To evaluate this multi-crystalline ingot property, the photovoltaic cells were made from this work's wafer. The measured cell properties on this work's cell were shown in Table 3[10-11]. The efficiency of cell exceeds 20%.
### Table 3 Cell properties

<table>
<thead>
<tr>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$</th>
<th>$Eff$ (%)</th>
<th>$Area$ (cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.9</td>
<td>634</td>
<td>0.782</td>
<td>18.3</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>37.7</td>
<td>664</td>
<td>0.809</td>
<td>20.3</td>
<td>4</td>
<td>11</td>
</tr>
</tbody>
</table>

4. Conclusion
In order to improve the conversion efficiency of the photovoltaic cell with multi-crystalline silicon, the influence of solidification conditions on the microstructure was investigated by the experimental measurement and the simulation. The temperature distribution indicated similar tendency on both experiment and simulation result. The large supercooling in crucible bottom was effective in enlarging the crystal grain size. High quality silicon ingot was consequently obtained by using regulation of rapid solidification rate in the crucible bottom. (For regulation of the silicon grain size, the method that controls the heat flux from initial stage at crucible bottom to several stage is called the Multi-Stage solidification controlling method (MUST method).)

The wafer (thickness 5mm, resistivity 0.65Ω-cm) sliced from the silicon ingots with rapid solidification condition was measured over 350μm as the top on the diffusion length. The lifetime of the wafers from the rapid solidified silicon ingot was approximately corresponded to the single crystalline silicon wafer. The conversion efficiency of the cell produced using this silicon wafer reached to 18.3% (cell area 25cm$^2$) and 20.3% (cell area 4cm$^2$).

Acknowledgement
This investigation was the results of the project “Development of the practical technology for high efficiency multi-crystalline silicon solar cells” supported by Solar-Grade Silicon Technology Research Association (SOGA) and sponsored by New Energy and Industrial Technology Development Organization (NEDO).

### Nomenclature
- $v$: velocity, m/sec
- $P$: pressure, Pa
- $\mu$: viscosity, Pa·sec
- $E$: internal energy, J
- $Q$: external energy, J
- $\rho$: density, kg/m$^3$

### Constant number
- Silicon density $\rho = 2530$ kg/m$^3$ at $T_m = 1683$ K
- Proportional constant $\rho_s = 0.35$
- Viscosity $\mu = 0.94$ mPa·sec
- Specific heat $c_p = 0.9683 \cdot 10^3$ J/(kg·K)
- Thermal conductivity $\lambda = 0.9683 \cdot 10^3$ W/(m·K)

### References