Growth of high quality Si multicrystals by controlling the arrangement of dendrite crystals and the density of random grain boundaries

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The world’s energy consumption is about **30TW** at 2002. It is only **0.04%** of the available solar energy.

Solar energy contributes to only **0.1%** of the world’s energy consumption. If we will use solar energy for **10%** of the world’s energy consumption (**1600 GW**) at 2050, we must manufacture about **40 GW** solar cells every year for 40 years.
Main material for solar cells is Si crystals except for First Solar.
Typical Japanese house

In the case of the conversion efficiency of solar cells of 15%:

2.6 men

(The energy consumption in Japanese house is about $4.5 \times 10^3$ kWh/person x year)

In the case of the conversion efficiency of solar cells of 20%:

3.5 men
The most important points to obtain high-quality Si multicrystals using crucibles

1. Purity control
2. Structure (grain size, grain orientation, grain boundary character) control
3. Crystal defect (dislocation, sub-brain boundaries) control
4. Stress control
The points of the purity control

1. Materials (Si sources, crucible, furnace---)

2. Prevent contaminations (gas flow-----)

This is very simple, but very difficult.
The points of the structure (grain size, grain orientation, grain boundary character---) control

Typical Si multicrystals

① Same grain orientation

② Electrically inactive grain characteristics

③ Proper grain sizes

Ideal Si multicrystals

Growth direction
The points of crystal defects (dislocation, sub-brain boundaries) control

Conventional casting method

Usually, sub-grain boundaries are generated from random grain boundaries during crystal growth.
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Newly developed *in situ* observation system

Temperature gradient in furnace

- 1414°C
  - (Melting point of Si)
- Temp. 0.4°C/mm
- 20 mm (±1°C)
- 20 mm
- 10 mm

**microscope**

**furnace**

**heater**

**silica crucible**
Crystals grown on Si \{111\} and \{100\} seeds from Si growth melt cooled at 30°C/min.
Cooled at 30°C/min

Si melt

1 mm

crucible
Dendrite crystal grows along the bottom of the crucible

A sharp and long needle-like crystal grows

Dendrite crystal

Si melt

~1 mm

t = 3[s]  t = 5[s]

t = 15[s]  t = 25[s]
Dendrite crystals appear when $\Delta T$ is larger than 10 °C.
The growth direction of the twins is exactly same as that of the dendrite crystal.

Two parallel twins with Σ3 grain boundaries with the same \{111\} facets.
Orientation of dendrite crystals depends on $\Delta T$

Supercooling of the Si growth melt $\Delta T$ (°C)
Structures of Si multicrystals grown by the two types of method

Conventional casting method

Dendritic casting method

Growth direction

Large grain

Bottom of the crucible

Growth direction of dendrite crystals
Si melt

Dendrite crystals grow along the bottom of the crucible

Si multicrystals grow on the upper surface of the dendrite crystals

Concept to control the grain orientation and the grain size

Cross sections of a Si multicrystal

Center

Bottom

Dendrite crystal
Using a 15 cmφ-crucible
Structures of Si multicrystals grown by the two types of method

Conventional casting method

Dendritic casting method

Larger grains

Smaller grains

50mmφ × 30mmH
The diffusion length distribution is not affected by dendrite crystals and grain boundaries like $\Sigma 3$. 
Si multicrystal with the same orientation

Si multicrystal with different orientations

Size of the crystal: 50mmφ

Conversion efficiency (%)

Distance from the bottom of the crystal (mm)
Si multicrystal ingot cut from a larger Si ingot with a diameter of 30cm and a high of 15 cm

$20\text{cm} \times 20\text{cm} \times 15\text{cm}$
Number of dendrite crystals as a function of the length of dendrite crystals

- The total number is 27.
- The average length is 6.2 cm.
- The maximum length is 18.2 cm.
多数のデンドライトの発現により結晶粒サイズが小さい

デンドライトの発現数の低下により結晶粒サイズが大幅に改善された
The most important points to obtain high-quality Si multicrystals using crucibles

1. Purity control
2. Structure (grain size, grain orientation, grain boundary character---) control
3. Crystal defects (dislocation, sub-brain boundaries----) control
4. Stress control
Relation between random grain boundaries and sub-grain boundaries during crystal growth

Conventional casting method

- Directional growth
- Crucible
- Si melt
- Random grain boundaries
- Many random grain boundaries
- Small grain size

Dendritic casting method

- Directional growth
- Crucible
- Twins
- Sub-grain boundaries
- Random grain boundaries
- Very few random grain boundaries
- Quite large grain size
A special seed crystal

Artificially manipulated grain boundary

Distribution of etch pit density of dislocations

Reflecting light from flat surface

Scattered light from etch pits
Distribution of shear stress near an artificially manipulated grain boundary

The side with generated dislocations corresponds to the side with larger shear stress.
There are many sub-grain boundaries with small angular difference near random grain boundaries.

X-ray rocking curve profiles around twin boundaries

A photo image of a Si wafer cut from a Si ingot parallel to the growth direction.

X-ray rocking curve profiles around random grain boundaries
Photo and photoluminescence images of Si wafers

**Photo image**

Grown by the conventional casting method

![Photo image of conventional casting method](image)

Grown by the dendritic casting method (effective to suppress sub-grain boundaries)

![Photo image of dendritic casting method](image)

**Photoluminescence image**

Grown by the conventional casting method

![Photoluminescence image of conventional casting method](image)

Grown by the dendritic casting method (effective to suppress sub-grain boundaries)

![Photoluminescence image of dendritic casting method](image)

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Sub-grain boundaries

10cm
Total length of the random grain boundary

Distance from the bottom of the ingot (cm)

- Conventional casting method
- Dendritic casting method

Effective to suppress sub-grain boundaries
Dislocation density strongly depends on coherency of grain boundary.
The most important points to obtain high-quality Si multicrystals using crucibles:

1. **Purity control**
2. **Structure** (grain size, grain orientation, grain boundary character---) control
3. **Crystal defect** (dislocation, sub-brain boundaries----) control
4. **Stress control**
Si multicrystal ingot with a diameter of 30cm and a high of 7 cm grown by the dendritic casting method

The bottom of the ingot

Dendrite crystal

10 cm
Distribution of large grains grown on dendrite crystals along the bottom of an ingot

The wafer size is 10 cm x 10 cm. It was cut from an ingot with 15 cm Φ.
Growth of dendrite crystals from Si melt
Quality of crystals solidified at the small melt region surrounded by crystals

PL image

Etch pits

Orientation image mapping

Many dislocations generated within this region and a twin boundary appeared as a grain boundary.
Distribution of dendrite crystals grown on the surface of Si growth melt

A large grain appeared from the top of the dendrite crystal

Flat grain boundaries are naturally formed where dendrite crystals collided with each other
Growth behavior when a dendrite crystal just collided with another crystal

The tip of the dendrite became flat because the heat of crystallization was kept between them.
Effect of the angle ($\Theta$) between dendrite crystals with several orientations

On the shear stress

On the dislocation density

Dendrite crystal

Grain boundary
Distribution of dendrite crystals grown along the bottom of an ingot with a diameter of 30cm
Arrangement of dendrite crystals grown along the bottom of the ingot
Most of dendrite crystals within the angle of ±50 degrees

Angle of dendrite crystals inclined from the y-axis (θ)
Si multicrystal ingot cut from a Si ingot with a diameter of 30cm and a high of 7 cm

20 cm × 20 cm × 7 cm
Wafer position in the Si ingot used for the preparation of solar cells

![Graph showing the level of Si single crystals (using the same solar cell process) at various positions along the ingot.](chart)

- **Conversion efficiency (%)**
- **Distance from the bottom of the ingot (cm)**

- Level of Si single crystals (Using the same solar cell process)

- **Height of ingot** 4.7 cm
- **Top** and **Bottom**
- **10 cm x 10 cm wafers were cut from the ingot.**
Conversion efficiency of solar cells with the same orientation

Level of Si single crystals
(Using the same solar cell process)

Evaluator (Wafer size)

A社 (15cmΦ: 100mm×100mm)

Height of the ingot: 4.7 cm

Distance from the bottom of the ingot (cm)
Manufacture a pilot furnace for industrial scale ingots - controlling the structure and contamination of crystals -

The size of a conventional crucible

~80 cm

The present Si multicrystal ingot

(Size: 30 cmΦ, 4.7 ~ 7.5 cm high)

High quality crystals can be obtained even using small crucibles by the dendritic casting method.
The most important points to obtain high-quality Si multicrystals using crucibles

1. Purity control
2. Structure (grain size, grain orientation, grain boundary character) control
3. Crystal defects (dislocation, sub-brain boundaries) control
4. Stress control
   “More natural growth” or “More Artificial growth”
Floating cast method

Nucleation

Si melt

Floating Si crystal

Si melt

“More natural growth” or “More Artificial growth”
Dendrite crystals

Floating Seed
Photographic image

Carrier diffusion length

Schematic illustration of the seed growth
Conclusions

- The most important points to obtain high-quality Si multicrystals using crucibles are the **purity, structure, crystal defect, and stress control.**
- Using dendrite crystals grown along the bottom of ingot gives effective solution to control the **structure and crystal defect** in Si multicrystals.
- Decreasing crystal defects such as sub-grain boundaries and dislocations affects is greatly important to obtain high-quality Si crystals. Main factors to decrease them are the density and coherency of random grain boundary, and stresses in crystals.
- The dendritic casting method is effective to control the grain boundary character and suppress sub-grain boundaries by controlling the arrangement of the distribution of dendrite crystals.
- We are manufacturing a pilot furnace for industrial scale ingots, which can control the structure of Si multicrystals.
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