Refining of Si by the Solidification with eutectic molten alloy at low temperature

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Background

Short supply of SOG-Si

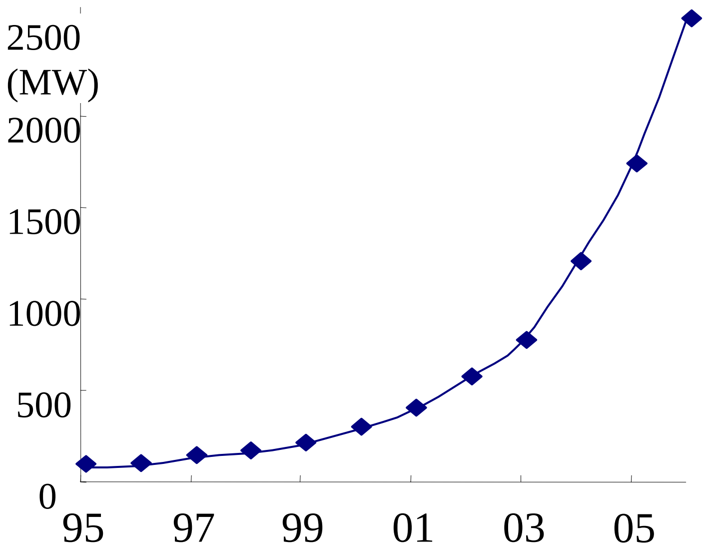
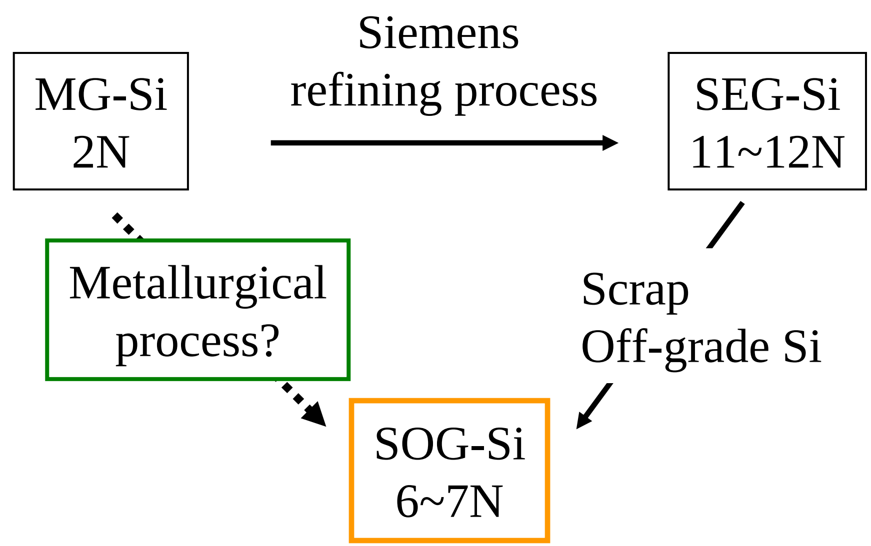


Fig. Production of Solar Cell



Depending on off-grade Si for semiconductor

Short supply of Si for solar cell

Source: PV News（April 2006）, JPEA (HPhttp://www.jpea.gr.jp/6/6-1.htm)

Metallurgical process
(NEDO SOG-Si manufacturing process)

MG-Si (2N)

First step

Vacuum melting by electron beam
(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)

SOG-Si (6~7N)

Fig. NEDO SOG-Si manufacturing process

Keeping at high temperature for a long time

Much low cost process

Methodology of Si refining by the solidification with eutectic molten alloy

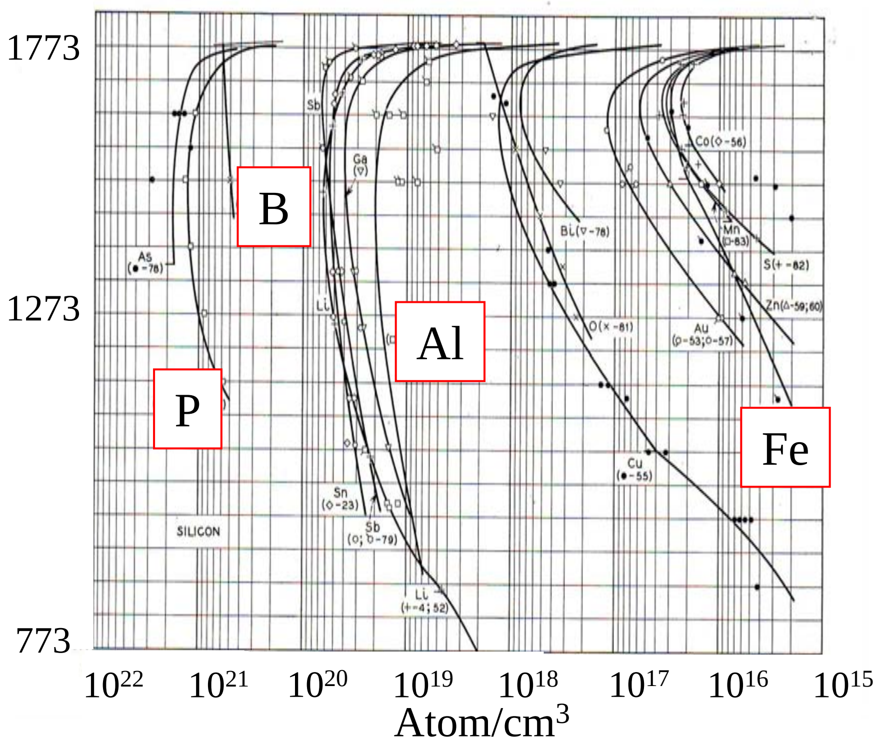


Fig. Solid solibilities of impurity elements in Si

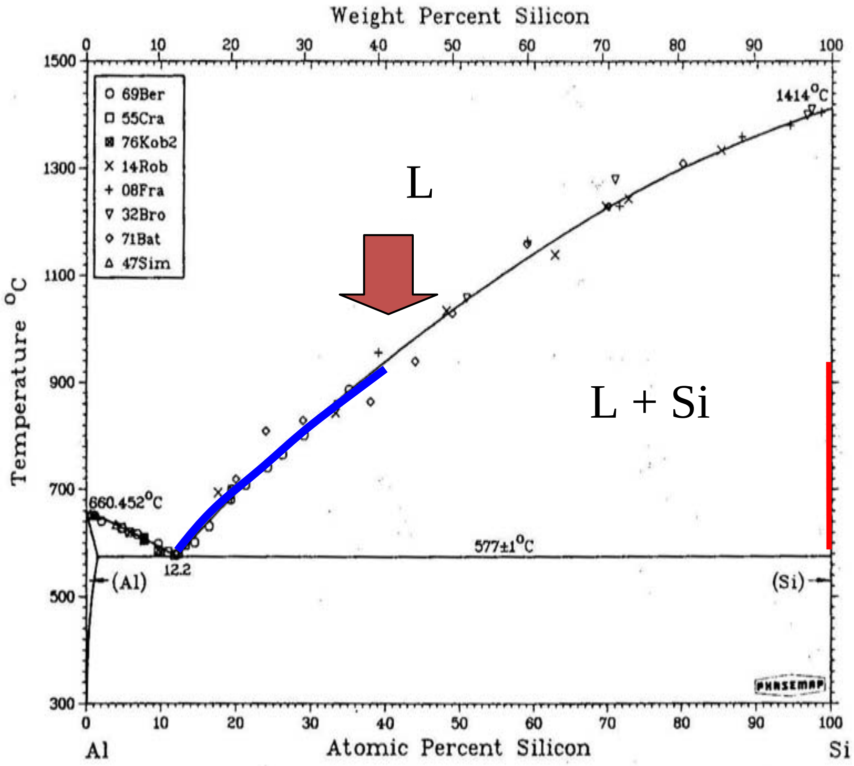


Fig. Phase diagram of Si-Al binary system

Possibility of Si refining at low temperature

Reference: J.L. Murray and A.J. McAlister, Bulletin of Alloy Phase Diagrams, 5 (1984), 74.

Segregation ratio and impurity contents

Table Segregation ratio of impurity elements

Elements	Between Si-Al melt and solid Si at 1273K	At m.p. of Si
Fe	5.9×10^{-9}	6.4×10^{-4}
Ti	1.6×10^{-7}	2.0×10^{-4}
P	8.5×10^{-2}	3.5×10^{-1}
B	2.2×10^{-1}	8×10^{-1}

Fe, Ti : Calculated from thermodynamic data
P, B : Actual measurement

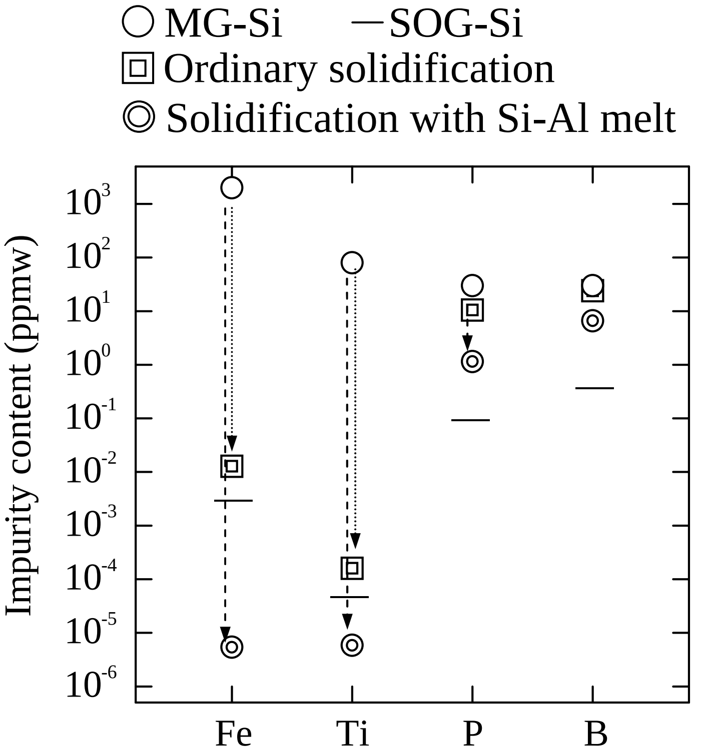


Fig. Contents of impurity elements

High purification ability of solidification with Si-Al melt

Reference: T. Yoshikawa, Doctor Thesis Univ. of Tokyo (2004)

Directional solidification

Growth rate 0.2 cm/min (5 K/cm,1 K/min) | 0.02 cm/min (50 K/cm,1 K/min)

Fig. Cross section of Si-55.3at%Al alloy after directional solidification

High dispersive refined Si in Si-Al melt

Objective of this work

Separation of refined Si from molten alloy

Experimental

Experimental procedure 1
(Separation with gravity force)

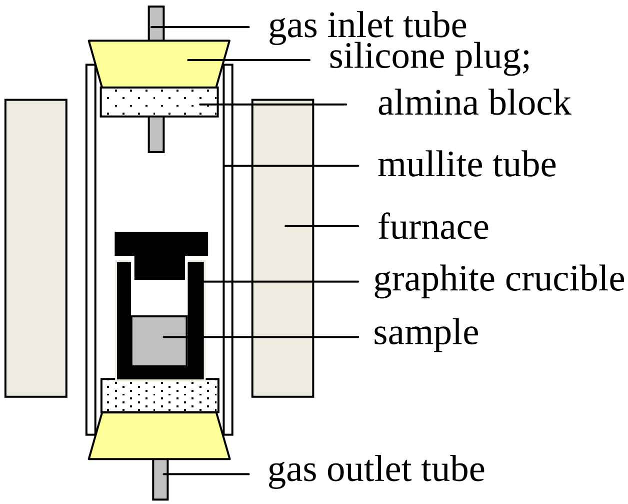


Fig. Experimental apparatus

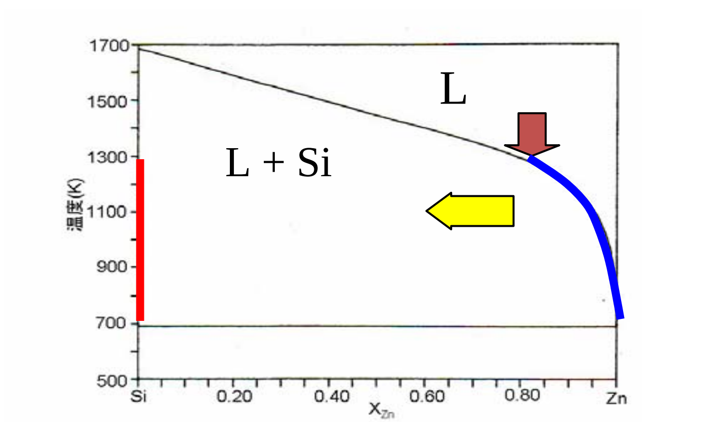


Fig. Phase diagram of Si-Zn system

Weighing
（Si-55.3at%Al, Si-95at%Zn）

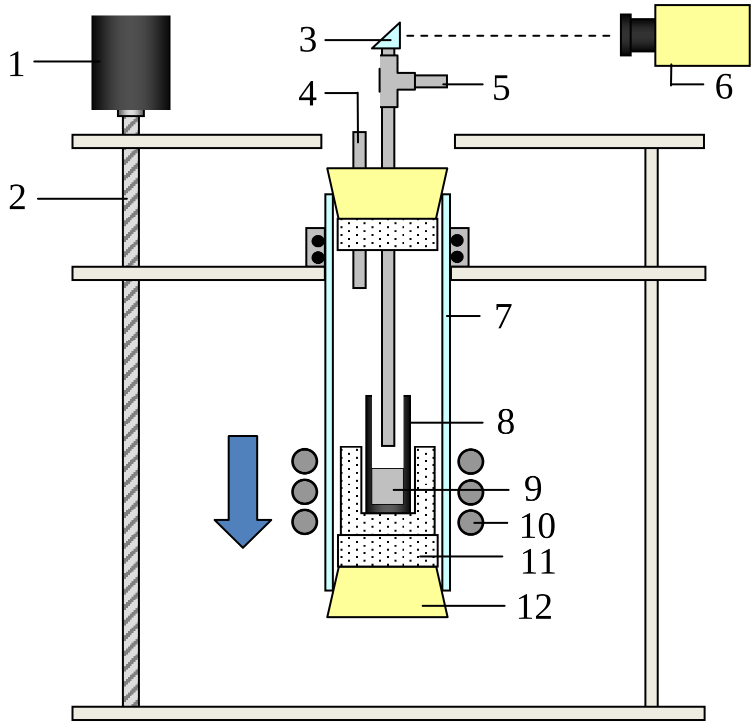
Melting and quenching

Flotation (1173K,12h)	Flotation (973K,0.5h)

Observation

Reference: S. an Mey and K.Hack: Z. Metallkd,1986,77(7),454-459

Experimental procedure 2
(Separation with magnetic force)



1—stepping motor; 2—ball screw; 3—prism;
4—gas outlet tube; 5—gas inlet tube;
6—pyrometer;7—quartz tube; 8—graphite crucible;
9—Si-Al melt; 10—induction coil;
11—porous alumina holder; 12—silicone plug

Fig. Experimental apparatus

Weighing (Si-55.3at%Al)

↓

Melting (1323K,10min)

↓

Solidification (Lowering rate :0.25-1.0 mm/min)

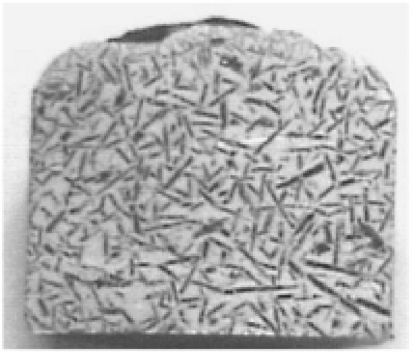
↓

Observation

Result and discussion

Separation with gravity force

Si-55.3at%Al

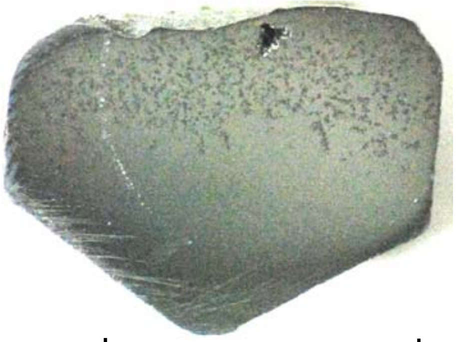


1cm

⊿ρ= 0.246 (g/cm³)

Si-95at%Zn

Top



1cm

⊿ρ= 4.801 (g/cm³)

Density (g/cm³) Si:2.328 Al:2.698 Zn:7.13

Fig. Cross section of samples

Si flotation in Si-Zn melt

Separation with magnetic force

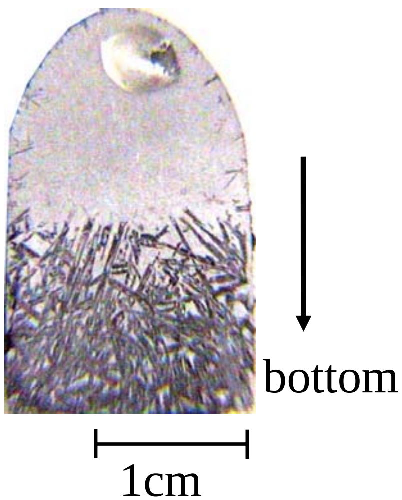


Fig. Cross section of sample (Si-Al)

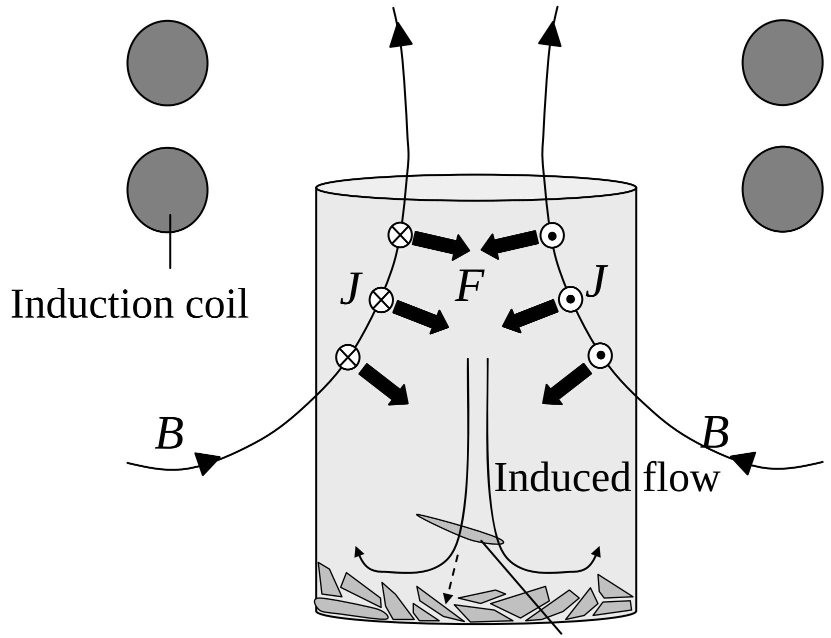


Fig. Mechanism for agglomeration of Si grains

Si grains were agglomerated at the bottom

Impurity contents in refined Si

Table Impurity contents in refined Si from Si-55.3at%Al melt
(ICP emission spectroscopy and Mo blue absorption spectroscopy)

Sample No.	Fe	Ti	Al	B	P
MG-Si	4500	691	1280	56	36
Refined Si 1	13	5.2	599	0.93	0.81
Refined Si 2	13	2.7	534	1.2	0.88

Confirmation of high purification ability

Conclusion

・Gravity force was effective for the separation of refined Si in Si-Zn melt, but not effective in Si-Al melt .

・Electromagnetic force was effective for separation of refined Si in Si-Al melt and Si grains were agglomerated at the bottom of melt.

・High purification ability of Si refining by the solidification with Si-Al melt was confirmed.