

Recovery of Si from liquid Si–Zn alloy using Si rod

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Abstract

As part of the development of a new production process for solar grade Si, a method for Si recovery from liquid Si–Zn alloys was investigated. It was found that Si could be recovered by using Si rod. The removal fraction of impurity elements from metallurgical grade Si was more than 99% for Al, Ti, and Fe, 97% for B and Ca and 86% for P, due to the solvent refining effect of the Si–Zn alloy.

High-purity Si, commonly used in crystalline Si solar cells, is referred to as solar-grade Si (SOG-Si) and typically has a purity level of 6–7 N. Currently, SOG-Si is produced via the Siemens process, which uses metallurgical-grade Si (MG-Si) obtained through the carbothermal reduction of SiO_2 . However, the Siemens process is limited by low production efficiency and high energy consumption.^[1] To address these limitations, several next-generation methods for SOG-Si production have been investigated. These include improving the Siemens process,^[2] the metallurgical purification of MG-Si,^[3–6] and the thermal reduction of Si halides using a metal-reducing agent.^[7] While promising, these alternatives also pose significant challenges. For instance, the metallurgical purification of MG-Si involves multiple complex and costly steps to effectively eliminate impurities and achieve the desired level of purity.

Our research group has investigated the feasibility of producing Si through the electrochemical reduction of SiO_2 using a liquid Zn electrode in a molten salt.^[8–11] Based on these findings, we have proposed a novel process for SOG-Si production, as illustrated in Fig. 1.^[12,13]

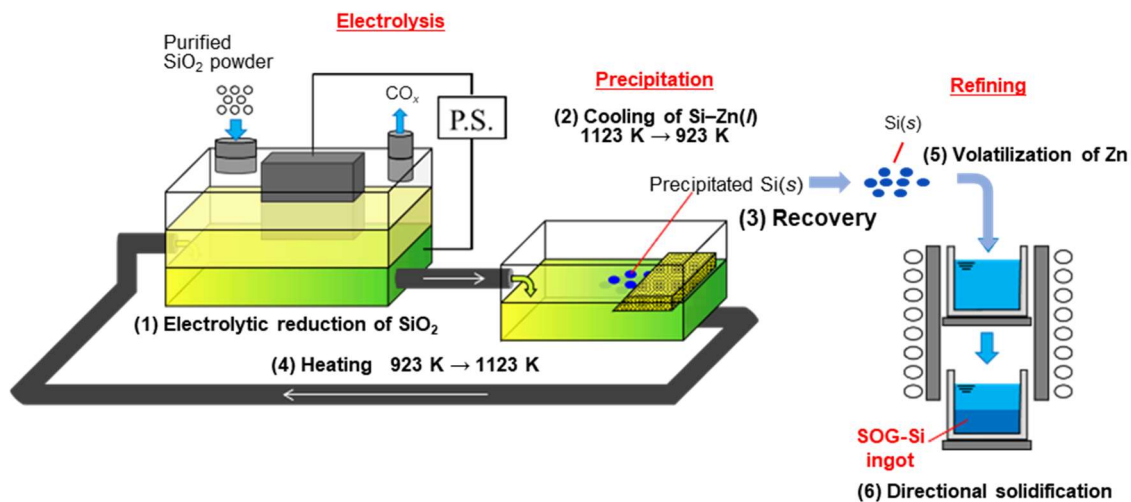


Fig. 1—Schematic illustration of the previously proposed pragmatic process for producing solar-grade Si. ^[12,13]

The proposed process (Fig. 1) consists of three principal stages: electrolytic reduction, precipitation, and refining. Among these, the precipitation stage has not yet been investigated in detail. In the present study, specific methodologies for the precipitation stage were examined to validate the practical feasibility of the overall process.

In the experimental investigation, a high-purity Si rod was immersed in a molten Si-Zn alloy. Subsequent cooling of the alloy induced the deposition of Si onto the surface of the high-purity Si rod, thereby enabling the recovery of Si from the Si-Zn alloy. To prevent contamination of the deposited Si, the purity of the Si rod must exceed that of the precipitating Si. Therefore, high-purity Si rods were employed in this study. Additionally, solvent refining of Si using the Si-Zn alloy at low temperatures was investigated. This approach leverages the thermodynamic instability of impurity elements in solid Si at lower temperatures. This phenomenon is expected from the retrograde solidus lines of impurities in Si.^[14] The solid solubility of Zn in Si at 1123 K has been reported to be

extremely low at 2.3×10^{-3} ppmw.^[15] Therefore, Zn is a promising metal for solvent refining. This study reports on both the recovery of Si from Si–Zn alloys and the solvent refining of MG-Si using Si–Zn alloy.

A graphite crucible (Toyo Tanso Co. Ltd., IG-110 grade, outer diameter: 100 mm, inner diameter: 90 mm, height: 150 mm) was charged with high-purity Zn (974 g, Mitsui Mining and Smelting Co. Ltd.), MG-Si (26.7 g, Japan Natural Energy & Resources Co. Ltd), CaCl_2 (240 g, FUJIFILM Wako Pure Chemical Co. Ltd., Reagent Grade, >95.0 %), and NaCl (119 g, FUJIFILM Wako Pure Chemical Co. Ltd., Reagent Grade, >99.5 %). The crucible containing the raw materials was initially dried under vacuum at 453 K for at least 24 h to eliminate residual moisture. Following the drying process, the crucible with the raw materials was placed at the bottom of an airtight container consisting of a quartz inner holder (inner diameter: 110 mm, height: 370 mm), a quartz outer holder (inner diameter: 127 mm, height: 400 mm), and a stainless-steel flange cover (diameter: 160 mm). Precipitation experiments were conducted using an electric furnace (outer diameter: 400 mm, inner diameter: 150 mm, height: 360 mm) controlled with a Shimaden FP23 temperature controller. The internal temperature was monitored using thermocouples placed within alumina tubes (Nikkato, SSA-S, outer diameter: 6.0 mm, inner diameter: 4.0 mm). Prior to experimentation, the crucible containing the raw materials was dried under vacuum at 653 K for a minimum of 10 h to ensure complete removal of residual moisture. To prevent thermal degradation of the O-rings that secured the flange cover and alumina tube, the upper section of the airtight vessel was air-cooled using a fan.

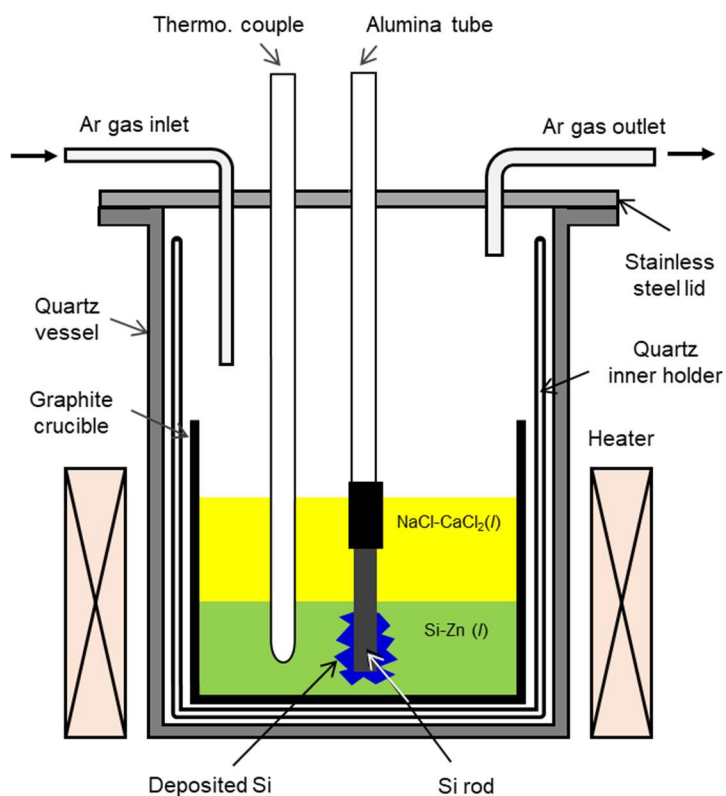
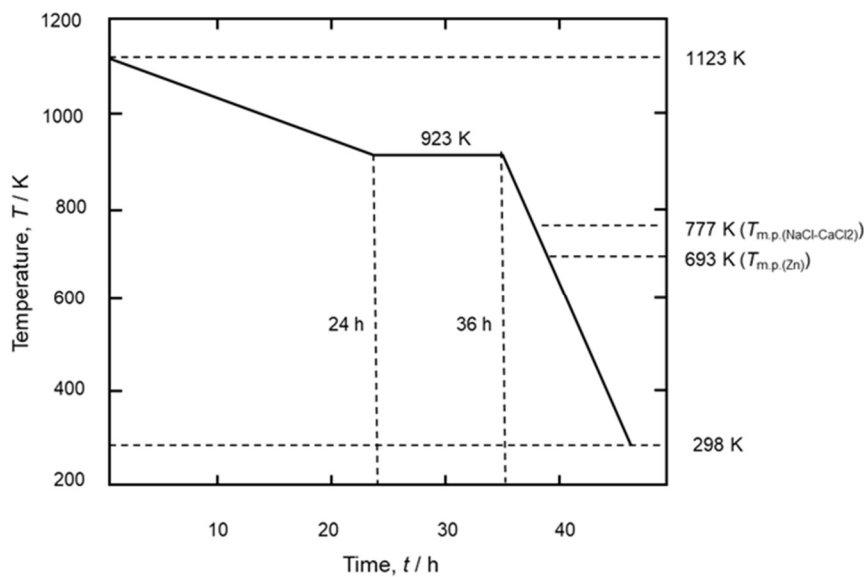


Fig. 2– Schematic illustration of the experimental apparatus used to recover Si from a liquid Si–Zn alloy.

Fig. 2 shows a schematic of the experimental apparatus employed to precipitate solid Si from a liquid Si–Zn alloy. The Si recovery experiments were conducted under an Ar atmosphere (Kyoto Teisan Co. Ltd., >99.998 %) with a continuous Ar flow rate of 50 mL min^{−1}. The Si–Zn alloy was melted at 1123 K. To facilitate the dissolution of MG-Si, molten Zn was stirred using alumina rods, as required, and maintained at 1123 K for 24 h. Following alloy preparation, high-purity Si rods (Furuuchi Chemical Co. Ltd., diameter: 6.0 mm, 99.999 %) connected to an Al₂O₃ tube and a graphite rod were submerged into the melt. Prior to immersion, the Si rods were pretreated with molten Zn to remove any surface oxide films. After immersion, the temperature of the molten bath was gradually decreased to induce the precipitation of solid Si on the rod surface.

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89 Fig. 3– Temperature changes during the cooling step in the recovery process of Si from a
 90 liquid Si–Zn alloy.

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92 Fig. 3 illustrates the temperature profile of the molten bath during the cooling phase for
 93 Si precipitation. The bath temperature was gradually decreased from 1123 to 923 K over
 94 24 h. After maintaining the bath at 923 K for an additional 12 h, the high purity Si rod
 95 was withdrawn. The liquid Si–Zn alloy was subsequently cooled to room temperature
 96 over a subsequent 10 h period. In this precipitation process, Si equivalent to 6 at% (the
 97 saturation concentration of Si at 1123 K) was added to Zn. Upon cooling to 923 K, the
 98 saturation concentration of Si decreases to 1 at%, resulting in the precipitation and
 99 recovery of Si equivalent to a 5 at% difference in the saturation concentration.

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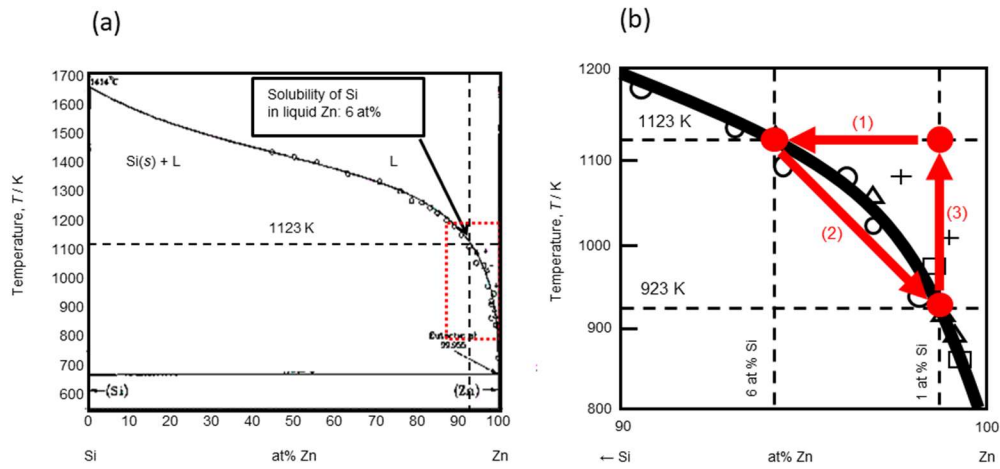


Fig. 4— (a) Phase diagram of the Si–Zn binary alloy.^[16] (b) Enlarged view of the high Zn concentration side. The three steps of the proposed process are indicated using arrows and numbered as (1)–(3).^[12]

Fig. 4 illustrates the phase diagram of the Si–Zn binary system,^[16] including an enlarged view of the high Zn concentration region, with arrows indicating the sequence of steps in the proposed process.^[12] Fig. 4(b) shows the relationship between the Si concentration in the molten bath and temperature across the three stages of the SOG-Si production process illustrated in Fig. 1. The three steps correspond to (1) the electrolytic reduction process, (2) the precipitation process, and (3) the reheating and recycling process.

Following the experiment, the withdrawn high-purity Si rod was rinsed with hot distilled water to dissolve and remove the residual solidified NaCl–CaCl₂ salt from its surface. Subsequently, the high-purity Si rod was treated with 20 wt% HCl to eliminate any adhered Zn. During this cleaning process, most of the Si particles deposited on the rod surface were detached and collected. The collected Si particles were subsequently treated overnight in a mixed acid solution containing 10 wt% HCl and 10 wt% HNO₃ to

remove other impurities from the surface. After acid treatment, the particles were thoroughly washed with distilled water and collected via filtration using a suction membrane filter. Remaining moisture was removed by drying the particles on a hot plate. The morphology of the deposited Si particles was examined using scanning electron microscopy (SEM; Phenom Pro Generation 5, Thermo Fisher Scientific Inc.). Additionally, the phase of the Si particles was identified using X-ray diffraction (XRD; Rigaku, Ultima IV, Cu- $K\alpha$ line, λ ; 1.5418 Å, 40 kV, 40 mA). The impurity concentrations in the deposited Si particles were analyzed by high-frequency inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Fig. 5(a) and (b) show the optical images of the Si particles precipitated on the high-purity Si rod (a) immediately after its withdrawal from the liquid Si–Zn alloy and (b) after being washed with hot distilled water to remove the solidified salts via dissolution. Further, Fig. 5(c) shows the high-purity Si rod washed with 20 wt% HCl, demonstrating that the adhered Zn was removed, and Fig. 5(d) shows the detached Si particles recovered after further washing with 10 wt% HCl and 10 wt% HNO₃, revealing that the maximum particle size of recovered Si was approximately 2–3 mm.

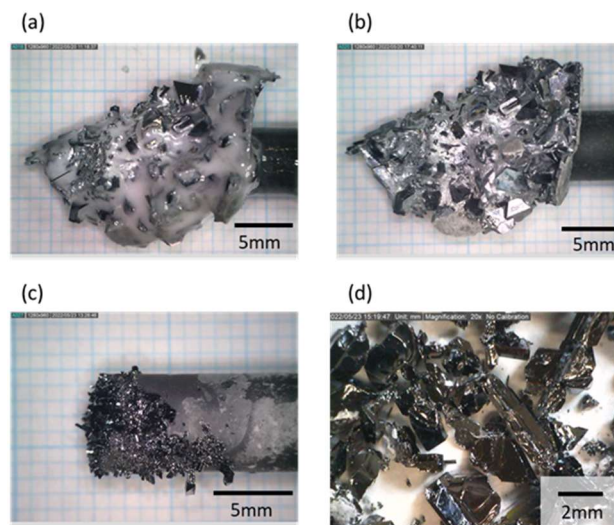


Fig. 5– Photographs of deposited Si: (a) Immediately after withdrawal from the liquid Si–Zn alloy, (b) after washing with hot water, and (c) after washing with 20 wt% aqueous HCl. (d) Detached Si particles after washing with 10 wt% HCl and 10 wt% HNO₃.

Most of the precipitated Si particles were readily detached from the high-purity Si rod, which is advantageous for enabling the rod's reuse in subsequent processing cycles. This detachment behavior is attributed to the weak adhesion between the high-purity Si rod and the precipitated particles. The yield of recovered Si, calculated based on the ratio of the recovered Si mass to the initial amount of Si added to the melt, was approximately 1.1%.

Fig. 6 presents the SEM images of the deposited Si particles, where angular shapes are clearly visible, indicating the good crystallinity of the particles.

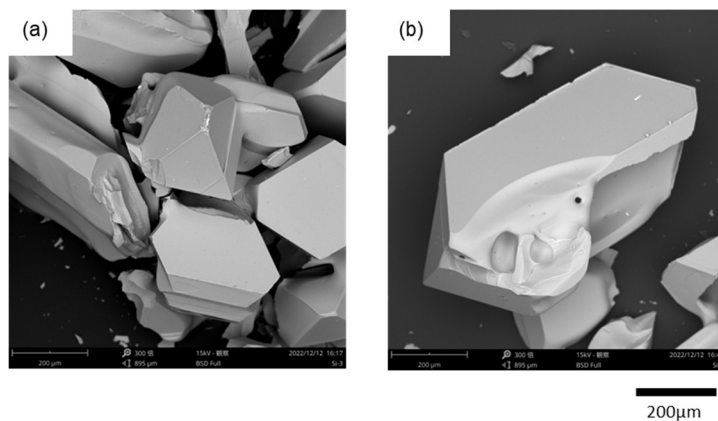


Fig. 6– SEM images of the deposited Si particles.

The XRD pattern of the deposited Si particles (Fig. 7) only shows the diffraction peaks of Si, confirming that the deposited particles are indeed Si crystals. For reference, a typical XRD pattern of powdered Si is also included.

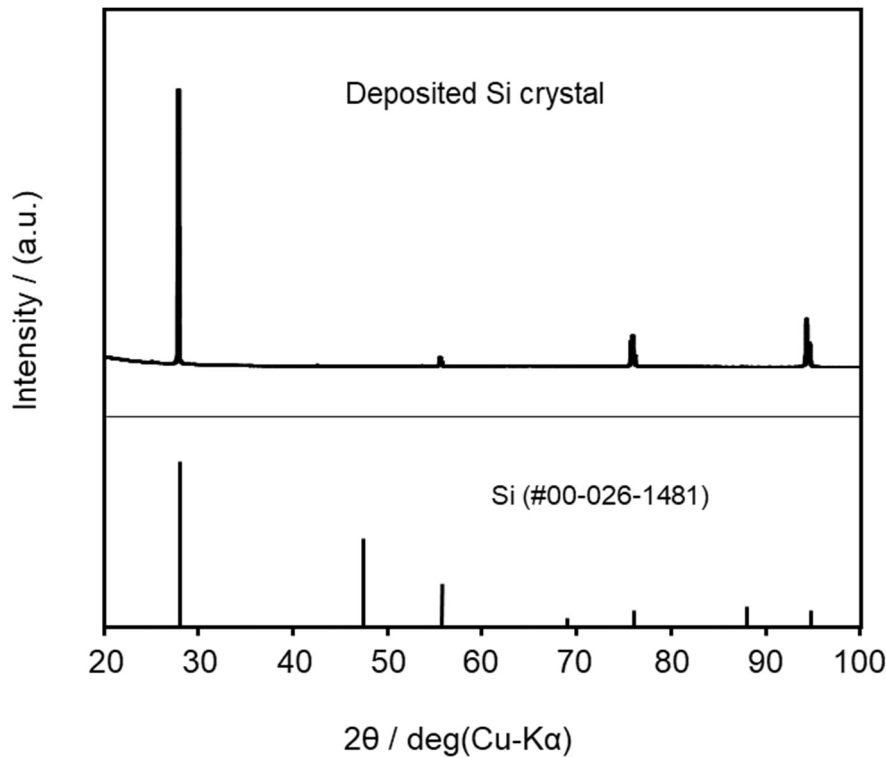


Fig. 7– XRD pattern of the deposited Si particles.

Table I presents the impurity concentrations of the Si particles recovered in this study, along with the removal fractions for each impurity element. For comparison, the impurity concentrations in MG-Si used as the raw material are also listed. All impurity concentrations were determined using ICP-AES. For reference, Table I also includes the impurity concentrations in the Si particles recovered from the liquid Si–Zn alloy using our previously reported method^[17], in which the entire Si–Zn alloy was treated with a 20 wt% HCl solution, and the remaining undissolved Si particles were subsequently recovered. Additionally, the acceptable impurity concentrations for SOG-Si as defined in

the literature^[18,19] are provided for context. The segregation coefficients of the respective impurity elements at the melting point of Si were obtained from the literature.^[14,20,21] In our proposed process (Fig.1), it was assumed that vacuum refining and directional solidification would be employed in the refining stage. Therefore, the target impurity concentration levels were estimated by dividing the acceptable impurity concentrations for SOG-Si by the corresponding segregation coefficients.^[13] Further, the removal fraction of impurity elements (r_A) was calculated using the impurity concentration in the MG-Si raw material, $x_{A(MG-Si)}$ and that in the precipitated Si, $x_{A(Rec Si)}$, using the following formula:

$$\gamma_A = \left(1 - \frac{x_{A(Rec. Si)}}{x_{A(MG-Si)}}\right) \times 100 \quad [1]$$

As shown in Table I, the concentrations of Al, Fe, and Ti in the Si particles recovered in this study were <1, 12, and <1 ppmw, respectively, with the removal fractions exceeding 99%. The concentrations of both B and Ca were <1 ppmw, achieving removal fractions of over 97%. The P concentration was 4 ppmw, with a removal fraction of 86.4%. These impurity concentrations were comparable to or lower than those obtained in our previous study,^[17] except for Zn. Notably, the P concentration was nearly one-tenth of that achieved in the previous method, which is remarkable given the challenges associated with removing P from Si.^[17] The reason for the decreased in P concentration is not clear and will be the subject of future research.

In this study, the concentrations of Al, Ca, Fe, and Ti in the recovered Si particles were lower than the target levels, indicating effective removal of these impurity elements. However, the concentrations of B and P remained above the target thresholds, due to the

extremely stringent purity requirements for these elements in SOG-Si. In our proposed process, Si is supplied to the liquid Si–Zn alloy by the electrolytic reduction of purified SiO₂, as illustrated in Fig. 1. In our previous study, the concentrations of B and P in the Si particles recovered through electrolysis were reported to be 1.3 ppmw^[22] and 0.39 ppmw,^[23] respectively; these concentrations are lower than those in MG-Si used as the raw material in this study. These results suggest that, by employing electrolytic reduction of purified SiO₂ as the starting material, the concentrations of B and P can be further reduced to meet the target levels required for SOG-Si.

As shown in Table I, the Zn concentration in the recovered Si was exceptionally high as 37000 ppmw. This Zn concentration is significantly higher than the solid solubility of Zn in Si at 1123 K (2.3×10^{-3} ppmw^[15]). This elevated concentration is attributed to the entrapment of Zn within Si particles. Recovered Si particles are further refined through vacuum refining and directional solidification as outlined in Fig.1. In our previous study^[17] it has been demonstrated that the removal of Zn from Si is relatively straightforward using the floating zone method. Although the Zn concentration in the deposited Si particles exceeds the solid solubility, it is expected to be removed in the next refining process by vacuum refining and directional solidification method.

208 **Table I** Impurity concentrations in Si particles obtained via the proposed method using metallurgical-grade silicon as the raw material,
209 along with removal fractions. For reference, the table also includes results from a previous method,^[17] acceptable impurity levels for solar-
210 grade Si,^[18,19] segregation coefficients of impurities in Si,^[14,20,21] and target impurity levels based on segregation coefficients.^[13]

Impurity Element A	Impurity content in Si ^a / ppmw (Removal fraction <i>r</i> _A ^b)			Acceptable solar- grade Si level ^[18,19] / ppmw	Segregation coefficient ^[14,20,21]	Target level ^[13] / ppmw
	Metallurgical grade Si	Recovered Si from liquid Si–Zn alloy				
		Present method	Previous method ^[17]			
B	44	<1 (>97.8%)	0.6	0.1–0.3	0.8 ^[14]	0.13–0.38
P	29	4 (86.4%)	32	0.03–0.14	0.35 ^[14]	0.086–0.4
Al	3449	<1 (>99.9%)	<0.5	<0.1	2 × 10 ⁻³ ^[14]	<50
Ca	40	<1 (>97.5%)	<0.5	<0.2	1.6 × 10 ⁻³ ^[20]	<125
Fe	2287	12 (99.5%)	13	<0.1	8 × 10 ⁻⁶ ^[14]	<12500
Ti	314	<1 (>99.7%)	<0.1	<0.001	2 × 10 ⁻⁶ ^[21]	<500
Zn	<1	37000 (-)	310	-	1 × 10 ⁻⁵ ^[14]	-

211 a: Analyzed by ICP-AES

212 b: $r_A = (1 - x_{A(\text{Rec. Si})} / x_{A(\text{MG-Si})}) \times 100$

Generally, the removal of residual solvent metals from Si after purification is a significant challenge in solvent refining methods. For example, in the solvent purification method using Si–Al alloys, approximately 400–600 ppmw of Al remains in the Si particles after solvent refining.^[24] Given the distribution coefficient of Al in Si is 2×10^{-3} ^[14], at least two directional solidification refining cycles are required to sufficiently remove this Al. Similarly, in the case of Si–Sn alloys, it has been reported that approximately 3000 ppmw of Sn remains,^[25] necessitating vacuum dissolution and directional solidification to eliminate the residual Sn. Thus, the removal of residual solvent metals is a critical issue.

To estimate the Zn concentration when the recovered Si is purified by vacuum distillation at 1×10^{-2} atm (1×10^3 Pa) which is often used in the industrial process, at the melting point of Si (1687 K). The vapor pressure of pure Zn (P_{Zn}^0) and that of pure Si (P_{Si}^0) were reported as 3×10^6 Pa and 5×10^{-2} Pa, respectively.^[26] As the P_{Zn}^0 is much higher than P_{Si}^0 , the total gas pressure is assumed to be only the vapor pressure of Zn. Thus, the following equation holds.

$$1 \times 10^3 \text{ (Pa)} = P_{\text{Zn}}^0 \times a_{\text{Zn}} = P_{\text{Zn}}^0 \times \gamma_{\text{Zn}} \times X_{\text{Zn}} \quad [2]$$

Here a_{Zn} is activity of Zn, γ_{Zn} is the activity coefficient of Zn, and X_{Zn} is the atomic fraction of Zn in Si–Zn alloy. Since γ_{Zn} is reported to be 1.47 at 1687 K,^[27] X_{Zn} is calculated to be 2.3×10^{-4} atomic fraction. This corresponds as 5.3×10^2 ppmw. When obtained Si is further purified by directional solidification, the Zn concentration of purified Si is calculated to be 5.3×10^{-3} ppmw by using the distribution coefficient of Zn (1×10^{-5}) at 1687 K.^[14] Since this value is low enough for SOG-Si, Zn is an promising

solvent metal as it can be effectively removed by vacuum distillation and directional solidification.

As described, the study confirmed that Si can be efficiently recovered by immersing high-purity Si rods into a liquid Si–Zn alloy and lowering the temperature of the molten bath. Consequently, the precipitation process illustrated in Fig. 1 can be replaced with the improved method depicted in Fig. 8. Given that the precipitated Si can be easily detached from the high-purity Si rod, the rod can be reused in subsequent cycles.

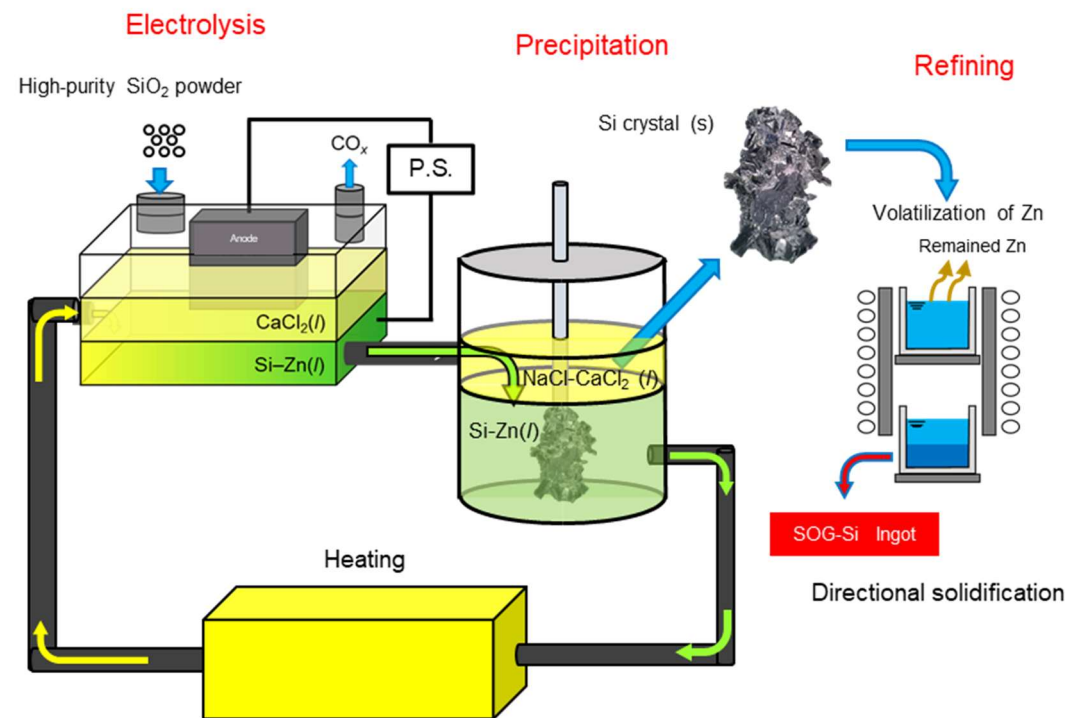


Fig. 8— Schematic illustration of the proposed new practical process for producing SOG-Si.

As a conclusion of this study, we investigated the recovery of Si from liquid Si–Zn alloys using high-purity Si rods to develop a new solar cell manufacturing process.

The results confirmed that Si can recover without solidifying the alloy. Also, from the point of solvent refining, Si–Zn alloy system is promising.

Acknowledgments

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Conflicts of Interest

The authors declare that they have no conflict of interest.

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Table captions

Table I

Impurity concentrations in Si particles obtained via the proposed method using metallurgical-grade silicon as the raw material, along with removal fractions. For reference, the table also includes results from a previous method¹⁶⁾, acceptable impurity levels for solar-grade Si^{18,19)}, segregation coefficients of impurities in Si^{14,20,21)}, and target impurity levels based on segregation coefficients¹³⁾.

Figure captions

Fig. 1. Schematic illustration of the previously proposed pragmatic process for producing solar-grade Si^{12,13)}.

Fig. 2. Schematic illustration of the experimental apparatus used to recover Si from a liquid Si–Zn alloy.

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