Removal of phosphorus by the solidification refining with Si–Al melts

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Abstract

To discuss the possibility of phosphorus removal from silicon by the solidification refining with Si–Al melts, the distribution of phosphorus between solid silicon and the liquid Si–Al alloy at 1173–1373 K was investigated. In the present study, the distribution of phosphorus was examined by the temperature gradient zone melting method, where a phosphorus containing molten Si–Al zone was passed through a single crystalline silicon phase. The segregation ratio of phosphorus at its infinite dilution was obtained as 0.12 (1373 K), 0.085 (1273 K) and 0.061 (1173 K), respectively, and the solidification refining with the Si–Al melts was found to be effective for the removal of phosphorus at lower temperature.

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Keywords: Silicon; Phosphorus; Si–Al; Segregation ratio; Activity coefficient; Temperature gradient zone melting; Solidification refining

1. Introduction

The amount of solar cell production, especially that of polycrystalline silicon, increases significantly with a growing demand for clean energy. Expensive off grade silicon for semiconductor (SEG-Si) has been a primary resource of polycrystalline silicon solar cell, but solar grade silicon (SOG-Si) would be short of supply with increasing demand for solar cell in the near future. Aiming at its cost reduction and the productivity increase, a new metallurgical refining process of SOG-Si using metallurgical grade silicon (MG-Si) as a starting material has been developed in Japan [1]. However, the development of much lower cost refining process is required for spreading solar cell widely.

Since the impurity elements in silicon possess the retrograde solidus curves [2], namely rapid decrease in solubility with temperature decrease much above the eutectic temperature, the removal of impurities from silicon at low temperature is expected to be effective. There are a few reports on low temperature techniques, such as silicon film growth processes by liquid phase epitaxy from the aluminum containing solvents [3–5] and solvent refining of MG-Si with Si–Al solvents [6,7], although the removal of impurities has not been considered thermodynamically in their discussions.

Phosphorus is one of the major impurities in silicon and should be reduced to lower than 0.1 ppmw for solar cell [8]. Since the segregation coefficient of phosphorus in silicon, 0.35 [9], is considerably larger than those of most metallic impurities in silicon, an ordinary solidification refining is less effective for the removal of phosphorus. On the other hand, phosphorus has high vapor pressure in molten Si [10] and the vacuum melting treatment has been employed in the newly developed process [1]. However, the vacuum melting refining process still requires a high temperature and long time operation. Shimpo et al. [11] investigated the removal of phosphorus by an acid leaching treatment with calcium addition and obtained the higher removal fraction of phosphorus with the larger amount of calcium addition. Therefore, alloying of silicon may bring the lower segregation ratio of phosphorus between solid silicon and the liquid alloy.

In order to clarify the possibility of phosphorus removal by the solidification refining with Si–Al melts, the segregation ratio of phosphorus between solid silicon and the liquid Si–Al alloy at 1173–1373 K was investigated in the present study. As both aluminum and phosphorus are low diffusive elements in solid silicon (e.g. phosphorus $6.5 \times 10^{-15}$ cm$^2$/s at 1273 K [12], aluminum...
4.0 \times 10^{-13} \text{ cm}^2/\text{s at 1273 K} \) [13]), solidification of silicon from the liquid Si–Al alloy was considered to be suitable for introducing these elements into solid silicon to equilibrium levels, and temperature gradient zone melting (TGZM) method [14] was employed as in the previous studies [15,16]. The segregation ratio of phosphorus between solid silicon and the liquid Si–Al alloy was determined by measuring phosphorus and aluminum contents of silicon in equilibrium with the liquid Si–Al alloy using electron probe microanalyzer (EPMA). Also, the phosphorus contents of the liquid Si–Al alloy saturated with AlP were investigated in order to understand the behavior of phosphorus in such melts.

2. Experimental

2.1. Phosphorus contents of the liquid Si–Al alloy saturated with AlP

A SiC electric resistance furnace connected to a PID controller with a Pt/6%Rh–Pt/30%Rh thermocouple was used for all the experiments in the present study. Two grams of Si–Al alloy and 0.5 g of a 50%Al–50%P pellet prepared by pressing the mixture of aluminum and red phosphorus powder at 800 MPa, were charged into a dense graphite crucible and closely packed with a dense graphite rod and ceramic bond, then held at the temperature ranging from 1173 to 1373 K for 12 h in an argon atmosphere. After equilibration, the sample was quenched, and the alloy was separated from the tablet and subjected to chemical analysis within 30 min to avoid the loss of phosphorus due to the reaction with moisture in air. The contents of aluminum and phosphorus were analyzed by ICP emission spectrometry and molybdenum blue absorption spectrometry, respectively.

2.2. Distribution of phosphorus between solid silicon and the liquid Si–Al alloy

Fig. 1 shows an experimental apparatus. The single crystalline silicon (11N purity) was cut into (111)-oriented plates of \(15 \times 15 \times 10\) and \(15 \times 15 \times 4\) mm\(^3\). After the plates were mechanically polished, an aluminum foil of 50 \(\mu\)m thick (99.9% purity) on which red phosphorus powder was stuck was located between two silicon plates and was fixed by a stainless steel holder. The holder on an alumina boat was placed at the part of 10 K/cm temperature gradient zone region in the furnace and held for 24 h at the temperature ranging from 1173 to 1373 K in an argon atmosphere. A few pieces of sponge titanium were also put on the alumina boat for the complete deoxidation of the atmosphere. Aluminum foil formed the molten Si–Al zone, which migrated in solid silicon toward the high temperature direction, leaving solidified silicon equilibrated with the melt. Migration distance of a molten zone was less than 500 \(\mu\)m, so temperature difference between initial and after the experiment was within 0.5 K. Moisture, oxygen, and CO\(_2\) in argon were removed by passing it through magnesium perchlorate, soda-lime and magnesium turnings heated at 823 K before the introduction to the furnace. During the experiments, temperature of a molten Si–Al zone was monitored by a Pt/6%Rh–Pt/30%Rh thermocouple located just above a molten zone.

Aluminum and phosphorus contents of the solid silicon were determined by the EPMA measurement with the accelerating voltage of 15 kV, sample current of 100 nA and counting time of 100 s. The deviations of the intensities of Al \(K_\alpha\) and P \(K_\alpha\) radiations were within ±2.5%. The intensities of Al \(K_\alpha\) radiation (8.338 \(\AA\)) and P \(K_\alpha\) radiation (6.159 \(\AA\)) in TGZM specimens were adjusted by subtracting those in a non-doped single crystalline silicon specimen as background. Pure aluminum was selected as a standard specimen for Al \(K_\alpha\) radiation, whereas SiP and Cu\(_3\)P were selected as standard specimens for P \(K_\alpha\) radiation. Aluminum and phosphorus contents of the samples in mass fraction were determined from the intensity ratios between a TGZM specimen and a standard specimen with ZAF correction.

In the case of the determination of phosphorus content of the molten zone, the remainder of the sample was subjected to chemical analysis. In order to determine only the molten zone of the sample, conc. HCl + HNO\(_3\) solution with slight addition of HF acid was used. Aluminum content was determined from the liquidus composition at the experimental temperature obtained from the Si–Al phase diagram [17], and phosphorus content was from the ratio of aluminum and phosphorus analyzed by ICP emission spectrometry and molybdenum blue absorption spectrometry, respectively.
3. Results and discussion

3.1. Phosphorus contents of the liquid Si–Al alloy saturated with AlP

From the X-ray diffraction pattern of the pellets after experiments, AlP was found to be the phosphide phase equilibrated with liquid alloys. The results for the phosphorus content of the liquid Si–Al alloy saturated with AlP at 1173–1373 K are summarized in Table 1 and Fig. 2. The open marks correspond to the experiments of doubly saturation with solid silicon and AlP. The phosphorus content slightly decreases or keeps an almost constant value with the increase in silicon content of the liquid alloy at each temperature. This means that the activity coefficient of phosphorus becomes larger with the increase in silicon content because the decrease in aluminum activity raises that of phosphorus at AlP saturation. Therefore, the segregation ratio of phosphorus between solid silicon and the liquid Si–Al alloy was expected to be smaller at the lower temperature where the aluminum content in the liquid Si–Al alloy equilibrated with solid silicon is larger.

3.2. Distribution of phosphorus between solid silicon and the liquid Si–Al alloy

The result of EPMA line analysis to the direction of a molten zone migration of the sample T16 is shown in Fig. 3. In the region of (b), where the molten Si–Al zone migrated during the experiments, the intensity profiles of Al Kα and P Kα radiation showed almost constant values. The vaporization loss of phosphorus during the TGZM was found to be negligible in spite of its high vapor pressure in the liquid alloy.

The experimental results for the phosphorus distribution between solid silicon and the liquid Si–Al alloy are summarized in Table 2. The relationship between segregation ratio of phosphorus and its content of the liquid alloy is shown in Fig. 4. The broken lines show the maximum contents of phosphorus in liquid alloy at each temperature determined in Section 3.1. The samples with the phosphorus contents of liquid alloy larger than the maximum contents are considered to contain AlP precipitates in the liquid alloy. Hence, the phosphorus contents of these samples were reduced to the maximum contents for the calculation of the segregation ratio of phosphorus in infinite dilution described later. The segregation ratio of phosphorus showed smaller values at lower temperature as expected. The values in Table 2 suggest that the aluminum content of solid silicon increases with the increase in the phosphorus content of solid silicon, indicating the strong affinity between aluminum and phosphorus in solid silicon. Accordingly, the interaction between these elements in solid silicon was evaluated by the following procedure. Since the variation in the phosphorus content is too small to affect the activity of aluminum in the liquid Si–Al alloy, the activity of aluminum in the liquid alloy is considered to be constant at each temperature. The activity of aluminum in solid silicon is also constant and Eq. (1) can be obtained.

\[
\ln \gamma_{Al}^{(s)} \text{ in solid Si} + \ln X_{Al} \text{ in solid Si} = \ln a_{Al}^{(s)} \text{ in liquid Si} = C_1 \text{(constant)}
\]

Table 1

| Sample no. | Temperature (K) | X_{Si} | X_{Al} | X_{P} |
|------------|-----------------|-------|-------|-------|
| P01        | 1373            | 0     | 0.996 | 0.0036|
| P02        | 1373            | 0     | 0.996 | 0.0043|
| P03        | 1373            | 0.355 | 0.642 | 0.0034|
| P04        | 1373            | 0.407 | 0.590 | 0.0018|
| P05        | 1373            | 0.557 | 0.440 | 0.0028|
| P06        | 1273            | 0     | 0.998 | 0.0018|
| P07        | 1273            | 0.263 | 0.735 | 0.0019|
| P08        | 1273            | 0.442 | 0.556 | 0.0019|
| P09        | 1173            | 0     | 0.999 | 0.0014|
| P10        | 1173            | 0.268 | 0.731 | 0.0013|
| P11        | 1173            | 0.345 | 0.654 | 0.0013|

Fig. 2. Phosphorus contents of the liquid Si–Al alloy saturated with AlP.

Fig. 3. Intensity profiles of Kα radiation of phosphorus and aluminum after the experiment for the sample No. T16 (accelerating voltage of 15 kV, sample current of 100 nA, sampling step of 3 mm).
In Eq. (1), the activity coefficient of aluminum in solid silicon can be expressed with the first order interaction parameters as expressed by Eq. (2)

$$
\ln g_{Al}^{\text{Si}} = \ln g_{Al}^{0} + e_{Al}^{\text{Al in solid Si}} X_{Al}^{\text{in solid Si}} + e_{Al}^{P in solid Si} X_{P}^{\text{in solid Si}}
$$

(2)

where $\ln g_{Al}^{0}$ is the activity coefficient of aluminum in solid silicon at infinite dilution relative to pure solid aluminum, and $e_{Al}^{\text{Al in solid Si}}$ and $e_{Al}^{P in solid Si}$ are the self-interaction parameter of aluminum and the interaction parameter between aluminum and phosphorus in solid silicon, respectively. Assuming that the self-interaction parameter can be neglected due to sufficiently small content of aluminum in solid silicon, Eq. (3) can be derived by combining and rearranging Eqs. (1) and (2).

$$
\ln X_{Al}^{\text{in solid Si}} = -e_{Al}^{P} X_{P}^{\text{in solid Si}} - \ln \gamma_{Al}^{\text{Si in solid Si}} + C_1
$$

(3)

Taking $\ln X_{Al}^{\text{in solid Si}}$ as the ordinate and $X_{P}^{\text{in solid Si}}$ as the abscissa, $-e_{Al}^{P}$ in solid Si can be derived from the slope of their linear relationship, which is shown in Fig. 5.

The intersects with the ordinate correspond to the solid solubilities of aluminum in silicon determined in the previous study [15] for the respective temperatures. Using the least-square method, $e_{Al}^{P}$ in solid Si was determined as $890 \pm 50$ (1373 K), $2100 \pm 200$ (1273 K) and $3000 \pm 500$ (1173 K), respectively. From the large negative value of the interaction parameter, the strong affinity between aluminum and phosphorus in solid silicon was confirmed. Considering that aluminum behaves as an acceptor while phosphorus as a donor in solid silicon, the bond between aluminum and phosphorus atoms could be strong for the electrical neutrality in solid silicon. The significant temperature dependence of $e_{Al}^{P}$ in solid Si can be explained by the relaxation of electrical stability of the Al–P bond in solid silicon at higher temperature, which is deduced from the fact that the release of electrons and holes from silicon atoms rapidly increases the conductivity of non-doped silicon with temperature increase.

### Table 2

Experimental results for distribution experiment of phosphorus between solid silicon and the liquid Si–Al alloy (#: undetected)

| Sample no. | Temperature (K) | $X_{P}^{\text{in solid Si}}$ | $X_{Al}^{\text{in solid Si}}$ | $C_{P}/C_{Al}$ in liquid alloy | $X_{P}^{\text{in liquid alloy}}$ | Segregation ratio, $k$ |
|------------|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------------|
| T01        | 1373            | 0.000076                    | 0.000456                    | 0.00176                     | 0.00070                     | 0.108               |
| T02        | 1373            | 0.000161                    | 0.000491                    | 0.00329                     | 0.00131                     | 0.123               |
| T03        | 1373            | 0.000195                    | 0.000492                    | 0.00397                     | 0.00158                     | 0.123               |
| T04        | 1373            | 0.000270                    | 0.000520                    | 0.00483                     | 0.00192                     | 0.140               |
| T05        | 1373            | 0.000346                    | 0.000537                    | 0.00616                     | 0.00245                     | 0.141               |
| T06        | 1373            | 0.000428                    | 0.000557                    | 0.01030                     | 0.00411                     | 0.104               |
| T07        | 1373            | 0.000432                    | 0.000582                    | 0.00950                     | 0.00377                     | 0.115               |
| T08        | 1273            | 0.000032                    | 0.000307                    | #                          | #                          | #                   |
| T09        | 1273            | 0.000126                    | 0.000385                    | 0.00276                     | 0.00135                     | 0.093               |
| T10        | 1273            | 0.000193                    | 0.000371                    | 0.00360                     | 0.00177                     | 0.109               |
| T11        | 1273            | 0.000195                    | 0.000355                    | 0.00360                     | 0.00177                     | 0.110               |
| T12        | 1273            | 0.000201                    | 0.000395                    | 0.00527                     | 0.00259                     | 0.078               |
| T13        | 1273            | 0.000208                    | 0.000454                    | 0.00630                     | 0.00309                     | 0.067               |
| T14        | 1273            | 0.000220                    | 0.000484                    | #                          | #                          | #                   |
| T15        | 1173            | 0.000033                    | 0.000199                    | #                          | #                          | #                   |
| T16        | 1173            | 0.000050                    | 0.000240                    | 0.00150                     | 0.00081                     | 0.062               |
| T17        | 1173            | 0.000072                    | 0.000211                    | 0.00200                     | 0.00110                     | 0.066               |
| T18        | 1173            | 0.000100                    | 0.000245                    | 0.00240                     | 0.00136                     | 0.073               |

Fig. 4. Relationship between the segregation ratio of phosphorus and $X_{P}^{\text{in liquid alloy}}$.  

Fig. 5. Relationship between $X_{P}^{\text{in solid Si}}$ and $\ln X_{Al}^{\text{in solid Si}}$. 

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To discuss the removal of phosphorus from MG-Si by the solidification refining with the Si–Al solvents, where the phosphorus content is much smaller than that in the present work, the segregation ratio of phosphorus at infinite dilution was evaluated. At equilibrium, chemical potentials of phosphorus in solid silicon and the liquid Si–Al alloy are equal. Taking the solid standard state of phosphorus in both phases, Eqs. (4) and (5) can be obtained

\[ RT \ln \alpha_{P(s)} \text{ in solid Si} = RT \ln \alpha_{P(a)} \text{ in liquid alloy} \]  

\[ \ln \gamma_{P(s)} \text{ in solid Si} + \ln X_{P} \text{ in liquid alloy} = \ln \gamma_{P(a)} \text{ in solid Si} + \ln X_{P} \text{ in liquid alloy} \]  

The phosphorus content of the liquid Si–Al alloy is so small that the change in the molar ratio \( X_{Si}/X_{Al} \) is considered to be negligible at each temperature. Therefore, the activity coefficient of phosphorus in the liquid alloy should be constant due to its small content. Taking the activity coefficient of phosphorus in solid silicon with the first order interaction parameters and neglecting the self-interaction parameter of phosphorus due to its sufficiently small content, the segregation ratio can be expressed as Eq. (6)

\[ \ln k_{P} = \ln \frac{X_{P} \text{ in solid Si}}{X_{P} \text{ in liquid alloy}} = \ln \frac{\gamma_{P(s)} \text{ in liquid alloy}}{\gamma_{P(s)} \text{ in solid Si}} - \varepsilon_{P} \text{ in solid Si} X_{Al} \text{ in solid Si} \]  

Here, \( \gamma_{P(s)} \) in liquid alloy is the activity coefficient of phosphorus in the Si–Al alloy at infinite dilution relative to pure solid state. In the condition of the infinite dilution of phosphorus, the relationship of Eq. (7) can be obtained from Eq. (6)

\[ \ln k_{P}^{*} = \ln \frac{\gamma_{P(s)} \text{ in liquid alloy}}{\gamma_{P(s)} \text{ in solid Si}} - \varepsilon_{P} \text{ in solid Si} X_{Al}^{*} \text{ in solid Si} \]  

Here, \( k_{P}^{*} \) denotes the segregation ratio of phosphorus at its infinite dilution, and \( X_{Al}^{*} \text{ in solid Si} \) corresponds to solid solubility of aluminum at each temperature. Subtracting Eq. (6) from Eq. (7), the relationship of the segregation ratios of phosphorus between its infinite dilution and experimental results can be derived as Eq. (8)

\[ \ln k_{P}^{*} = \ln k_{P} + \varepsilon_{P}^{Al} \text{ in solid Si} (X_{Al} \text{ in solid Si} - X_{Al}^{*} \text{ in solid Si}) \]  

Thus, \( k_{P}^{*} \) can be obtained from the experimental values and \( \varepsilon_{P}^{Al} \text{ in solid Si} \) (= \( \varepsilon_{P}^{Al} \text{ in solid Si} \)) as demonstrated in Fig. 6.

Taking the averages, the value of \( k_{P}^{*} \) may be obtained as 0.12 (1373 K), 0.085 (1273 K) and 0.061 (1173 K), and this indicates the effective removal of phosphorus by the solidification refining with the Si–Al solvents, compared with the ordinary solidification refining at the melting point of silicon where the segregation coefficient of phosphorus is 0.35 [9].

3.3. Removal of phosphorus from silicon by the zone melting with Si–Al melts

Herewith, a quantitative consideration on the removal of phosphorus from silicon by the zone melting with the Si–Al solvent is performed. The molten Si–Al zone of the length \( l \) is assumed to pass through the silicon rod containing 30 ppm phosphorus. Providing that the diffusion of phosphorus and aluminum in solid silicon can be ignored and the composition is uniform in the molten zone, the material balance of phosphorus with the infinitesimal zone travel \( dx \) at solidified silicon length \( x \) can be expressed by Eq. (9)

\[ l \frac{dX_{P}}{dx} = (X_{P}^{0} \text{ in solid Si} - X_{P} \text{ in solid Si}) dx \]  

With the segregation ratio of phosphorus, Eq. (9) is rearranged as Eq. (10)

\[ \frac{dX_{P}}{dx} \frac{X_{P}^{0} \text{ in solid Si}}{X_{P}^{0} \text{ in solid Si} - X_{P} \text{ in solid Si}} = \frac{k_{P}}{l} dx \]

Taking the interaction between phosphorus and aluminum into consideration, the segregation ratio of phosphorus can be expressed as Eq. (12) with the relationship of Eq. (8)

\[ k_{P} = k_{P}^{*} \exp \left\{ \varepsilon_{P}^{Al} \text{ in solid Si} X_{Al}^{*} \text{ in solid Si} \right\} \]  

Substituting Eq. (11) into Eq. (10), the relationship between the phosphorus content of solidified silicon and solidified length can be obtained by integration as Eq. (12)

\[ \int_{x=0}^{x} \frac{X_{P}^{0} - X_{P}}{X_{P}^{0} \text{ in solid Si}} k_{P}^{*} \exp \left\{ \varepsilon_{P}^{Al} \text{ in solid Si} X_{Al}^{*} \text{ in solid Si} \right\} \frac{dX_{P}}{X_{P}^{0} \text{ in solid Si} - X_{P} \text{ in solid Si}} = \frac{x}{l} \]
The initial phosphorus contents of the molten zones are calculated to be 16.8 ppma (1373 K), 13.5 ppma (1273 K) and 11.0 ppma (1173 K) from the liquidus composition in equilibrium with solid silicon from the Si–Al phase diagram [17]. The relationship between the phosphorus content of the solidified silicon and the solidified length is shown in Fig. 7. Removal fraction of phosphorus and the treatable amount of silicon with aluminum to various solidified lengths are summarized in Table 3. Calculated results suggest that zone melting processes, including the TGZM method, would be effective for the phosphorus removal.

Also, the removal of phosphorus by the directional solidification of Si–Al melt can be predicted. It was considered that silicon containing 30 ppma phosphorus was alloyed with various amount of pure aluminum and Si-64.6 at.%Al, Si-55.3 at.%Al and Si-44.8 at.%Al alloys whose liquidus temperatures are 1173, 1273 and 1373 K, respectively, were directionally solidified. Assuming that the diffusion of phosphorus and aluminum in solid silicon can be ignored and the composition is uniform in the molten zone, distribution of phosphorus between solid silicon and the Si–Al melt during solidification is represented as Eqs. (13) and (14) by Scheil’s equation [18]

\[
(1 - f_s) dX_P \text{ in liquid alloy} = (X_P \text{ in liquid alloy} - X_P \text{ in solid Si}) df_s
\]

(13)

\[
\frac{dX_P \text{ in liquid alloy}}{X_P \text{ in liquid alloy}} = \frac{1 - k_P}{1 - f_s} df_s
\]

(14)

Here, \( f_s \) is the fractional solidification. It is considered that the segregation ratio represented by Eq. (15) obtained from the data in Section 3.2 by the least-square method could be applicable down to the eutectic temperature because of the sufficiently small phosphorus content.

\[
\ln k_P = 1.83 - \frac{5430}{T}
\]

(15)

The fractional solidification of each alloy can be calculated from the liquidus line [17] and lever rule as a function of temperature and is represented as Eqs. (16)–(18), respectively.

\[
f_s = 1.819 - 4.731 \times 10^{-3}T + 5.262 \times 10^{-6}T^2 - 2.174 \times 10^{-3}T^3
\]

(16)

(Si-64.6 at.%Al)

\[
f_s = 2.084 - 5.211 \times 10^{-3}T + 5.667 \times 10^{-6}T^2 - 2.246 \times 10^{-3}T^3
\]

(17)

(Si-55.3 at.%Al)

\[
f_s = 3.119 - 7.852 \times 10^{-3}T + 8.093 \times 10^{-6}T^2 - 2.934 \times 10^{-3}T^3
\]

(18)

(Si-44.8 at.%Al)

Substituting Eqs. (15)–(18) into Eq. (14), the phosphorus content of liquid phase can be obtained at temperature \( T \). When solidification is stopped at \( T \) and the liquid part is removed, the removal fraction of phosphorus can be calculated from Eq. (19) and is drawn in Fig. 8. Also, the removal fraction together with the required amount of aluminum and the loss of silicon is summarized in Table 4 when solidification is performed down to the eutectic temperature and the eutectic part is

| Temperature | 1173 K | 1273 K | 1373 K |
|-------------|--------|--------|--------|
| Solidified length | l | 3l | 5l | l | 3l | 5l | l | 3l | 5l |
| Average content of phosphorus (ppma) | 1.57 | 3.25 | 4.72 | 2.30 | 4.36 | 6.11 | 3.59 | 6.25 | 8.33 |
| Removal fraction of phosphorus (%) | 94.8 | 89.2 | 84.3 | 92.3 | 85.5 | 79.6 | 88.0 | 79.2 | 72.2 |
| Treatable amount of Si with 1 kg Al (kg) | 2.67 | 8.00 | 13.3 | 2.15 | 6.45 | 10.8 | 1.77 | 5.31 | 8.85 |
Estimated removal fraction of P
\[ \frac{X_{\text{final}}}{X_{\text{initial}}} = \frac{1}{2} f_{\text{final}} \]

\[ \text{Initial P in liquid alloy} \]
\[ \text{Final P in liquid alloy} \]
\[ \text{(1373 K), 0.085 (1273 K) and 0.061 (1173 K). The interaction parameters between phosphorus and aluminum in solid silicon, } \varepsilon_{\text{Al}}^p \text{ in solid Si, were determined as 890 ± 50 (1373 K), 2100 ± 200 (1273 K) and } -3000 \pm 500 \text{ (1173 K), and the strong affinity between phosphorus and aluminum in solid silicon was clarified. Calculated results revealed the effective removal of phosphorus by solidification refining process with the Si–Al melts such as zone melting or directional solidification.} \]

**4. Conclusion**

Phosphorus contents of the liquid Si–Al alloys equilibrated with AIP and the segregation ratio of phosphorus between solid silicon and the liquid Si–Al alloy at 1173–1373 K were investigated. The segregation ratio of phosphorus at its infinite dilution were obtained as 0.12 (1373 K), 0.085 (1273 K) and 0.061 (1173 K). The interaction parameters between phosphorus and aluminum in solid silicon, \( \varepsilon_{\text{Al}}^p \) in solid Si, were determined as 890 ± 50 (1373 K), 2100 ± 200 (1273 K) and -3000 ± 500 (1173 K), and the strong affinity between phosphorus and aluminum in solid silicon was clarified. Calculated results revealed the effective removal of phosphorus by solidification refining process with the Si–Al melts such as zone melting or directional solidification.

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