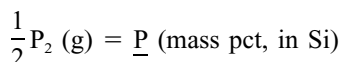


Thermodynamics of Phosphorus in Molten Silicon

TAKAHIRO MIKI, KAZUKI MORITA, and NOBUO SANO

Removal of phosphorus is one of the major problems on the purification of molten silicon for solar cell. The Gibbs energy change of phosphorus dissolution into molten silicon was determined in the temperature range from 1723 to 1848 K by equilibrating a molten silicon-phosphorus alloy in a controlled phosphorus partial pressure and is expressed by the following equations.



$$\Delta G^\circ = -139,000 (\pm 2000) + 43.4 (\pm 10.1T) \text{ (J/mol)}$$

The possibility of removing phosphorus from silicon melts by vacuum treatment and the accompanying yield of silicon during the refining process are discussed.

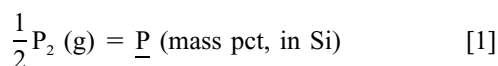
I. INTRODUCTION

SOLAR energy will shortly be in great demand, since it is inexhaustible and cleaner than any conventional energy resources. At present, expensive off-grade silicon for semiconductor (SEG-Si) is used for a solar cell to convert solar energy into electricity. For this reason, the solar cell system has not been developed widely until now. Using relatively inexpensive metallurgical grade silicon (MG-Si) as a starting material for making solar grade silicon (SOG-Si) is believed to be one of the ways to make solar cell less expensive.

Phosphorus is a typical impurity in silicon, and the required maximum limit for phosphorus content is 10^{-5} [mass pct P] for SOG-Si. Unfortunately, the segregation coefficient of phosphorus in silicon is large (0.35), so it is difficult to remove phosphorus by zone or unidirectional refining. Although some attempts to remove phosphorus by vacuum treatment have been carried out,^[1,2] quantitative analysis has not been made due to lack in thermodynamic properties of phosphorus in molten silicon. In the present study, the Gibbs energy change of phosphorus dissolution into silicon was determined by using a chemical equilibration technique.

II. EXPERIMENTAL

A molten silicon-phosphorus alloy was equilibrated in a controlled phosphorus partial pressure. The dissolution reaction of phosphorus into silicon and its Gibbs energy change are expressed by Eqs. [1] and [2], respectively.



$$\Delta G^\circ = -RT \ln \frac{f_p \cdot [\text{mass pct P}]}{p_{P_2}^{1/2}} \quad [2]$$

where R is the gas constant, f_p is the activity coefficient of phosphorus in liquid silicon relative to 1 mass pct, and p_{P_2} is the partial pressure of phosphorus. At low phosphorus concentration, the activity coefficient of phosphorus, f_p , may be assumed as unity.

The Gibbs energy change of phosphorus dissolution can be calculated by measuring phosphorus content of silicon at constant temperature and phosphorus partial pressure according to Eq. [2]. Temperature dependence of the Gibbs energy change has been measured from 1723 to 1848 K.

Ten grams of silicon-phosphorus alloy in a graphite crucible (30-mm o.d., 25-mm i.d., and 60-mm length) or 3g of silicon-phosphorus alloy in an alumina crucible (16-mm o.d., 14-mm i.d., and 55-mm length) was held in a graphite holder and equilibrated at temperatures ranging from 1723 to 1848 K controlled within ± 0.5 K in a deoxidized argon and phosphorus gas mixture. A portion of the sample was withdrawn by sampling by a quartz tube and was subjected to chemical analysis. Phosphorus content of silicon was analyzed by spectrophotometry. Equilibration time was determined as 1.51×10^2 ks by preliminary experiment.

Silicon-phosphorus alloy was prepared by the following procedure. After melting high-purity polycrystalline silicon in a graphite crucible, red phosphorus (purity 98 pct) wrapped in a paraffin paper was added to the melt and held for an hour.

Phosphorus vapor was generated by the transportation method, heating red phosphorus at a constant temperature (398 to 443K) and constant argon flow rate (3.17×10^{-6} m³/s STP) in a glass tube, and was controlled to have a constant partial pressure. In this temperature range, phosphorus is stable as tetratomic gas. Actual phosphorus partial pressure was calibrated by two methods.

The first one is by absorbing phosphorus gas into a bromine water at room temperature. From the mass of phosphorus in the bromine water determined by spectrophotometry and the argon flow rate, the phosphorus partial pressure at room temperature, p_{P_4} (Pa), was determined as follows.

$$p_{P_4} \text{ (room temperature)} = 1.86 \times 10^4 \cdot \frac{W \cdot T}{t \cdot V} \quad [3]$$

Here, W (kg) is the weight of phosphorus absorbed in bromine water, T (K) is the room temperature, t (s) is the

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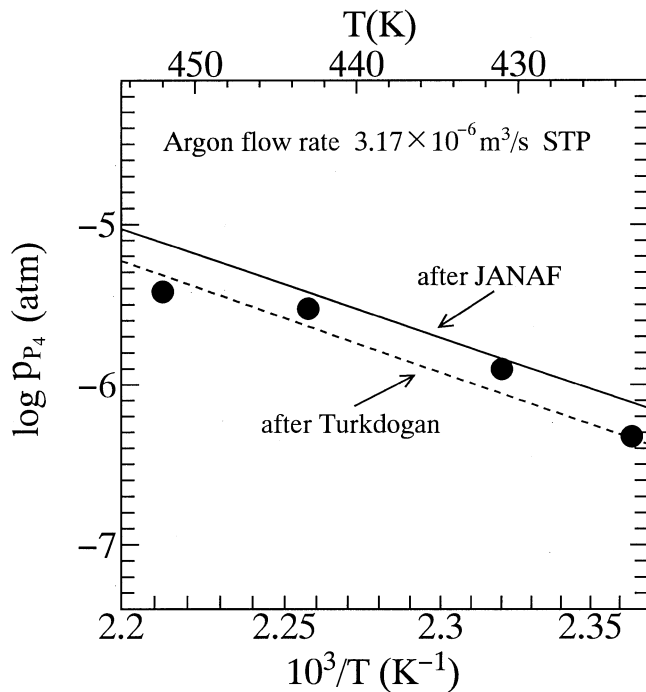


Fig. 1—Temperature dependence of phosphorus partial pressure which equilibrates with red phosphorus.

Table I. Phosphorus Content of Silicon Equilibrated with Phosphorus Gas between 1723 and 1848 K

Number	T (K)	p_{P_2} (Pa)	[Mass Pct P]	Crucible
1	1823	0.00859	0.0151	alumina
2	1823	0.0104	0.0185	graphite
3	1823	0.0331	0.0317	alumina
4	1823	0.206	0.0637	graphite
5	1823	0.357	0.0893	graphite
6	1823	0.492	0.110	alumina
7	1723	0.0212	0.0375	graphite
8	1723	0.0114	0.0330	graphite
9	1748	0.0209	0.0300	graphite
10	1748	0.0111	0.0283	graphite
11	1773	0.0206	0.0274	graphite
12	1773	0.0108	0.0229	graphite
13	1798	0.0107	0.0219	graphite
14	1848	0.00999	0.0148	graphite

absorbing time, and V (m^3/s STP) is the argon flow rate. At the experimental temperature, tetratomic phosphorus gas decomposes into diatomic and monatomic phosphorus gas. Hence, partial pressure of diatomic phosphorus gas in the system, p_{P_2} (Pa), can be determined using the following equations.

$$p_{P_4} (\text{room temperature}) = \frac{1}{2}p_{P_2} + \frac{1}{4}p_P \quad [4]$$

$$\frac{1}{2}P_2 (g) = P (g) \quad [5]$$

$$\Delta G^\circ = 248,000 - 59.4T(\text{J/mol})^{[3]} \quad [6]$$

The second one is by equilibrating phosphorus gas with molten silver at the same temperature with that for silicon. From the equilibrium phosphorus concentration of silver

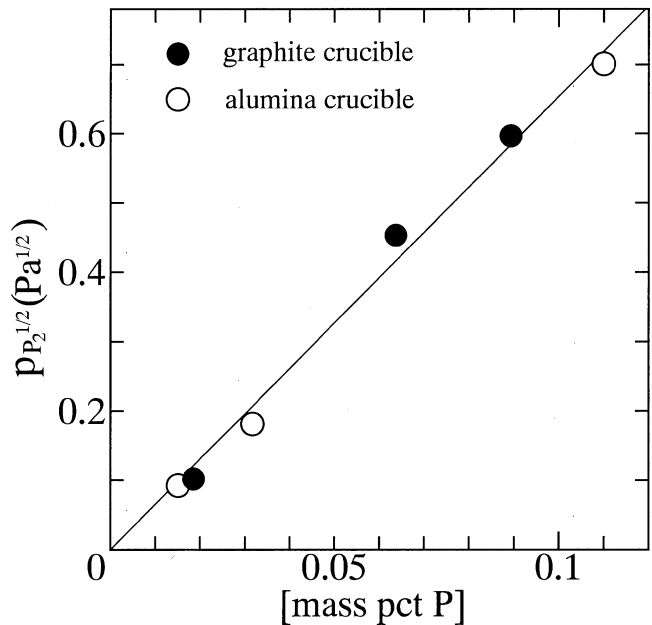


Fig. 2—Relationship between equilibrium phosphorus partial pressure and phosphorus concentration of silicon at 1823 K.

and Gibbs free energy change of phosphorus dissolution into silver,^[4,5] the phosphorus partial pressure, p_{P_2} , was determined.

It was confirmed that the values for phosphorus partial pressure obtained by respective ways are compatible with the thermodynamic properties of p_{P_4} , p_{P_2} , and p_P .^[3] Hence, it was ensured that the equilibrium between tetratomic, diatomic, and monatomic phosphorus gas was established at experimental temperatures. The relationship between the temperature of red phosphorus and phosphorus partial pressure is shown in Figure 1 together with that calculated from thermodynamic data^[3,6] for comparison.

III. RESULTS

The experimental results are listed in Table I. The relationship between partial pressure of phosphorus and phosphorus concentration of silicon at 1823 K is shown in Figure 2. A linear relationship in Figure 2 confirms that Henry's law is valid up to around 0.1 [mass pct P] and the activity coefficient of phosphorus in silicon is unity within the experimental range. Also, it was shown that the difference of the crucible used did not affect the results. The temperature dependence of Gibbs energy change of phosphorus dissolution into silicon is shown in Figure 3. Using the least-squares method, the Gibbs energy change of Reaction [1] is expressed as Eq. [7].

$$\frac{1}{2}P_2 (g) = \underline{P} (\text{mass pct, in Si})$$

$$\Delta G^\circ = -139,000 (\pm 2000) + 43.4 (\pm 10.1T) (\text{J/mol}) \quad [7]$$

where the values in the parentheses are standard deviations.

Combining with Eq. [6], the Gibbs energy change of monatomic phosphorus gas dissolution into silicon can be calculated as

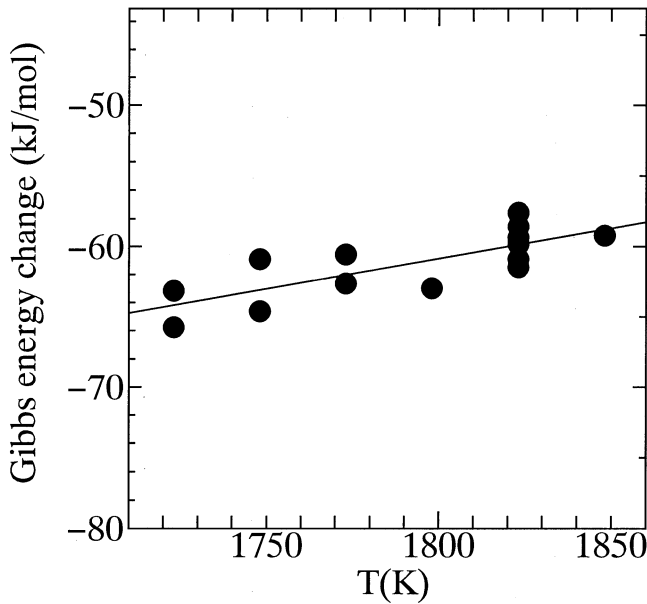


Fig. 3—Temperature dependence of the Gibbs energy change of phosphorus dissolution into silicon.

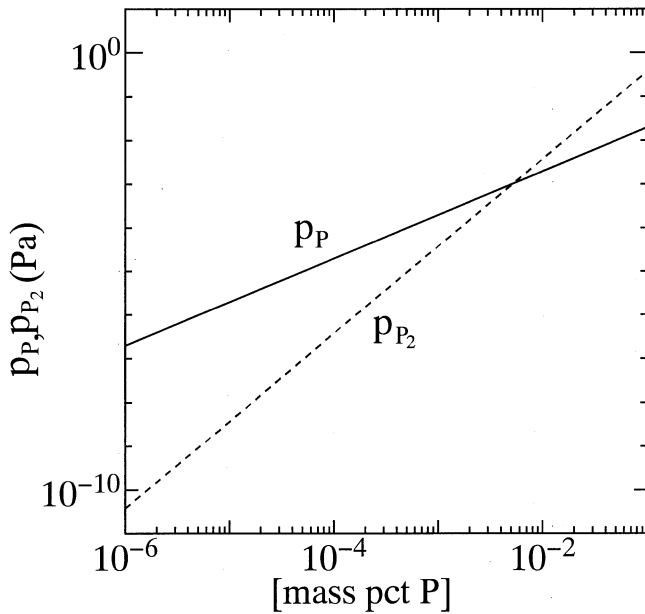


Fig. 4—Relationship between equilibrium partial pressure of P, P₂, and phosphorus concentration of silicon at 1823 K.

$$P(g) = \underline{P}(\text{mass pct, in Si}) \quad [8]$$

$$\Delta G^\circ = -387,000 (\pm 2000) + 103 (\pm 10T) \text{ (J/mol)} \quad [9]$$

If the activity of phosphorus is relative to the infinitely dilute solution of liquid silicon on a mole fraction basis, Eq. [11] is derived from Eq. [9].

$$P(g) = \underline{P}(X, \text{ in Si}) \quad [10]$$

$$\Delta G^\circ = -387,000 (\pm 2000) + 142 (\pm 10T) \text{ (J/mol)} \quad [11]$$

IV. DISCUSSION

The relationship between phosphorus content of silicon and phosphorus partial pressure at 1823 K is shown in Fig-

ure 4. At phosphorus concentration of silicon below 0.005 [mass pct P], monatomic phosphorus vapor is dominant in the gas phase.

Quantitative consideration concerning vacuum treatment can be done as follows. Let us now consider a melt initially containing A g of silicon and B g of phosphorus, and after vacuum was applied, x g of silicon and y g of phosphorus were evaporated. We only consider the case in which monatomic phosphorus vapor is a predominant species in the gas phase. According to Oletté,^[7] Eq. [12] can be obtained.

$$\frac{y}{B} = 1 - \left(1 - \frac{x}{A}\right)^\alpha \quad [12]$$

where

$$\alpha = \sqrt{\frac{M_{\text{Si}}}{M_{\text{P}}}} \cdot \frac{\gamma_{\text{P}}^0 p_{\text{P}}^0}{p_{\text{Si}}^0}$$

Here, M_{Si} and M_{P} represent the atomic weight of silicon and phosphorus; p_{P}^0 is the partial pressure of monatomic phosphorus, which is in equilibrium with pure liquid phosphorus; p_{Si}^0 ^[6] is the partial pressure of silicon, which is in equilibrium with pure liquid silicon; and γ_{P}^0 is the Raoultian activity coefficient of phosphorus. Here, $\gamma_{\text{P}}^0 p_{\text{P}}^0$ is identical to the partial pressure of monatomic phosphorus obtained by extrapolation from a dilute solution to pure liquid phosphorus using Eqs. [10] and [11].

For a dilute solution, content of phosphorus will be reduced if the evaporation coefficient, α , satisfies $\alpha > 1$. If $\alpha < 1$, phosphorus will concentrate. The value of α at 1823 K is actually 65.9, using $p_{\text{Si}}^0 = 0.312$ Pa and $\gamma_{\text{P}}^0 p_{\text{P}}^0 = 21.6$ Pa, and this indicates that phosphorus can be removed from silicon effectively by vacuum treatment. Furthermore, substituting this value for the evaporation coefficient α into Eq. [12], 90 pct of phosphorus could be eliminated when silicon evaporation loss is about 4 pct, for example.

In addition, the relationship between yield of silicon and phosphorus concentration during vacuum treatment can be calculated assuming that equilibrium is established between gas and liquid phases and that the phosphorus concentration is uniform throughout the melt. The yield of silicon, $1 - (x/A)$, can be obtained as follows. Equation [12] can be rewritten as Eq. [13].

$$1 - \frac{x}{A} = \left(\frac{B - y/A - x}{B/A}\right)^{1/(\alpha-1)} \quad [13]$$

When $B - y \ll A - x$ and $B \ll A$ are satisfied, Eq. [13] can be approximated as Eq. [14]

$$1 - \frac{x}{A} = \left(\frac{C_{\text{fin}}}{C_{\text{ini}}}\right)^{1/(\alpha-1)} \quad [14]$$

where C_{ini} is the initial phosphorus concentration, C_{fin} is the phosphorus concentration after vacuum treatment, and α is the evaporation coefficient. The relationship between yield of silicon and attained phosphorus concentration at 1823 K is shown in Figure 5. Initial phosphorus concentration of silicon was assumed to be 2.5×10^{-3} [mass pct P], which is the typical phosphorus concentration of MG-Si. During the reduction of phosphorus concentration from 2.5×10^{-3} [mass pct P] to 1.0×10^{-3} , 1.0×10^{-4} , and 1.0×10^{-5} [mass pct P] at 1823 K, the yield of silicon will be 98.6,

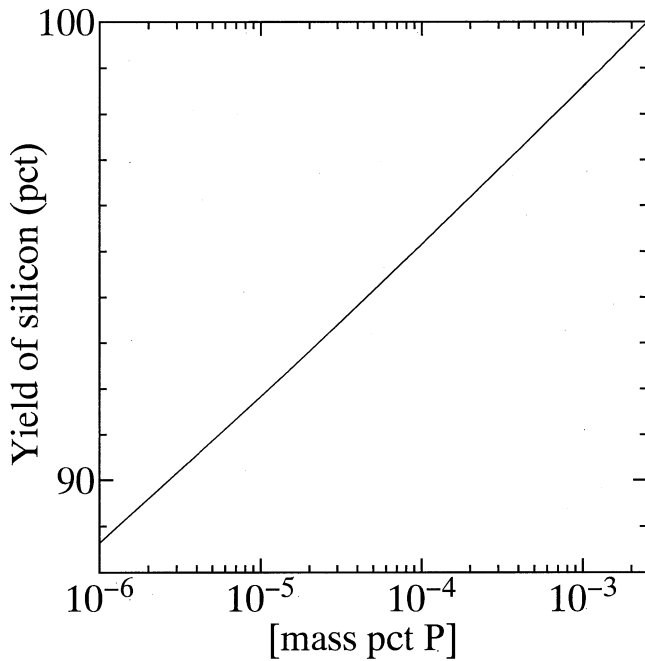


Fig. 5—Relationship between yield of silicon and attained phosphorus content at 1823 K with initial phosphorus content of 2.5×10^{-3} [mass pct P].

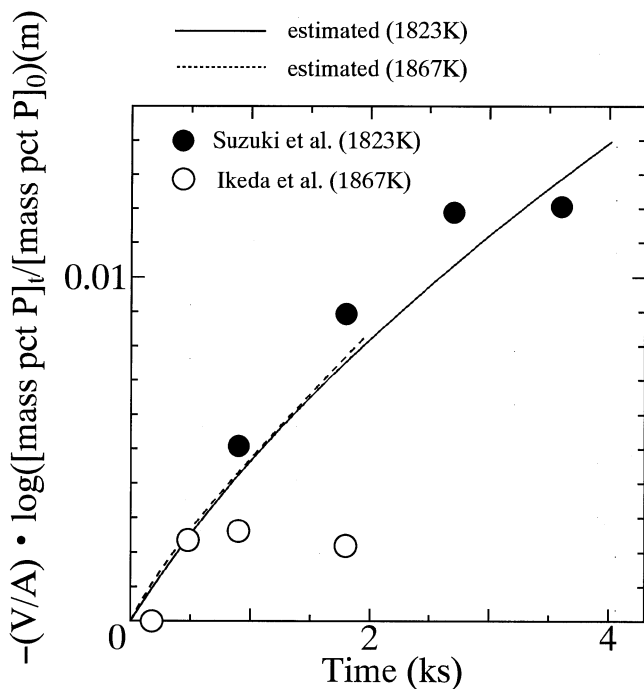


Fig. 6—Relationship between time for vacuum treatment and $-(V/A) \cdot \log ([\text{mass pct P}]_t / [\text{mass pct P}]_0)$.

95.2, and 91.8 pct, respectively. Furthermore, the yield of silicon slightly decreases with increasing temperature.

The evaporation kinetics of phosphorus during vacuum treatment will be discussed subsequently. If free evaporation controls the overall reaction rate, the evaporation rate of phosphorus in vacuum in terms of weight, W_p ($\text{kg}/\text{m}^2 \cdot \text{s}$), is expressed by Eqs. [15] and [16].^[7]

$$W_p = 4.37 \times 10^{-3} \cdot p_p \cdot \sqrt{\frac{M_p}{T}} \quad [15]$$

$$W_{p_2} = 4.37 \times 10^{-3} \cdot p_{p_2} \cdot \sqrt{\frac{M_{p_2}}{T}} \quad [16]$$

Equations [15] and [16] can be rewritten as Eqs. [17] and [18].

$$W_p = k_1 \cdot \frac{\rho_{\text{Si}}}{100} \cdot [\text{mass pct P}] \quad [17]$$

$$W_{p_2} = k_2 \cdot \left(\frac{\rho_{\text{Si}}}{100} \cdot [\text{mass pct P}] \right)^2 \quad [18]$$

Here, k_1 ($=4.43 \times 10^4 \cdot \sqrt{M_p/T} / \{\exp(-\Delta G^\circ_9 / RT) \cdot \rho_{\text{Si}}\}$) (m/s) and k_2 ($=4.43 \times 10^6 \cdot \sqrt{M_{p_2}/T} / \{\exp(-\Delta G^\circ_7 / RT) \cdot \rho_{\text{Si}}^2\}$) (m/s) are the rate constants of phosphorus evaporation at the silicon surface, where ΔG°_7 and ΔG°_9 are the Gibbs energy change of Eqs. [7] and [9] and ρ_{Si} is the density of silicon (kg/m^3). Using the density of silicon, $\rho_{\text{Si}} = 2.48 \times 10^3 \text{ kg}/\text{m}^3$ (1823 K), $2.46 \times 10^3 \text{ kg}/\text{m}^3$ (1867 K),^[8] the rate constants at 1823 and 1867 K, which are the temperatures employed by other investigators^[1,2] for vacuum treatments, are calculated as $k_1 = 4.55 \times 10^{-6} \text{ m/s}$ (1823 K), $8.28 \times 10^{-6} \text{ m/s}$ (1867 K) and $k_2 = 2.56 \times 10^{-3} \text{ m/s}$ (1823 K), $3.18 \times 10^{-3} \text{ m/s}$ (1867 K). If we neglect the silicon evaporation loss, the rate of phosphorus concentration change will be

$$\frac{d [\text{mass pct P}]}{dt} = -\frac{A}{V} (k_1 [\text{mass pct P}] + k_2 [\text{mass pct P}]^2) \quad [19]$$

Rearranging and integrating Eq. [19], Eq. [20] can be deduced.

$$\begin{aligned} [\text{mass pct P}]_t &= \frac{k_1}{-k_2 + \left(k_2 + \frac{k_1}{[\text{mass pct P}]_0} \right) \cdot \exp\left(\frac{A}{V} k_1 t\right)} \end{aligned} \quad [20]$$

where $[\text{mass pct P}]_0$ is the initial phosphorus concentration, $[\text{mass pct P}]_t$ is the phosphorus concentration at time t (s), A (m^2) is the surface area exposed to vacuum, and V (m^3) is the volume of silicon.

The relationship between $-\frac{V}{A} \cdot \log \frac{[\text{mass pct P}]_t}{[\text{mass pct P}]_0}$ and time is shown in Figure 6 together with experimental results for comparison.^[1,2] The estimation agrees well with the experimental results for removing phosphorus from silicon by vacuum treatment, indicating that free evaporation is a rate controlling step for phosphorus evaporation at the early stage of vacuum treatment.

IV. CONCLUSIONS

By equilibrating molten silicon-phosphorus alloy in a controlled phosphorus partial pressure at temperatures ranging from 1723 to 1848 K, the Gibbs energy change of phosphorus dissolution into silicon was determined as follows:

$$\frac{1}{2} \text{P}_2 (\text{g}) = \underline{\text{P}} (\text{mass pct, in Si})$$

$$\Delta G^\circ = -139,000 (\pm 2000) + 43.4 (\pm 10.1T) \text{ (J/mol)}$$

The present results can explain the experimental results in removing phosphorus from silicon by vacuum treatment, assuming that free evaporation is a rate controlling step. It is concluded that vacuum treatment is one of the promising refining processes of MG-Si.

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