High Temp. Mater. Proc., Vol. **31** (2012), pp. 73–81
DOI 10.1515/HTMP.2011.143

Kinetics and Mechanism of Phosphorus Removal from Silicon in Vacuum Induction Refining

Jafar Safarian[1,*] **and Merete Tangstad**[1]

[1] Norwegian University of Science and Technology,
Trondheim, Norway

Abstract. Vacuum induction refining is a process that can be applied to remove phosphorus from molten silicon for the production of solar grade silicon. Pure silicon was doped by phosphorus to make molten silicon containing around 17 ppmw phosphorus. The kinetics of phosphorus removal from this silicon was studied at 0.5 Pa through the application of vacuum induction refining. It was observed that vacuum removal of phosphorus occurs through a first-order reaction. The rate constants of phosphorus evaporation were determined as 2.28×10^{-6} m/s and 4.93×10^{-6} m/s at 1500 °C and 1600 °C, respectively. Moreover, an apparent activation energy 213.1 kJ/mol for phosphorus evaporation from molten silicon was calculated. It was found that mass transfer of phosphorus in the melt is not rate limiting in the inductively stirred silicon melt. The vacuum removal of phosphorus is mix-controlled by chemical reaction and gas phase mass transfer. Under medium vacuum conditions, the mass transfer in the gas phase is more rate-limiting than the chemical reaction at higher refining temperatures.

Keywords. Silicon, phosphorus, kinetics, mechanism, vacuum induction refining.

PACS®(2010). 81.20.Ym, 82.20.Pm, 88.40.jj.

1 Introduction

Silicon is the main element used for the fabrication of solar cells and with regard to the great solar energy demands it becomes a very important element in the 21st century. Traditionally, the scrap of the ultra-pure electronic-grade silicon (EG-Si) produced by Siemens process has been used for photovoltaic applications. The high cost of the EG-Si and also lower purity requirements for solar-grade silicon (SoG-Si) has motivated many research works to develop new processes for the production of SoG-Si through metallurgical routes. The main challenge in silicon purification through any metallurgical process is the elimination of boron and phosphorus, because their removal through directional solidification, which is considered as a key process step, is very difficult due to their large distribution coefficients. Vacuum refining technique can be considered as a process step in any metallurgical route for SoG-Si production in which the volatile elements and in particular phosphorus are removed.

From thermodynamics point of view, the difference between the vapour pressures of liquid silicon and the dissolved phosphorus is the basic principle for vacuum separation of phosphorus from silicon. The relationship between the saturated pressure of these elements and temperature (T) can be shown as [1]:

$$\log p^{\circ}_{\mathrm{Si}}\ (\mathrm{Pa}) = \frac{-20\,900}{T} - 0.565 \log T + 12.905, \tag{1}$$

$$\log p^{\circ}_{\mathrm{P}}\ (\mathrm{Pa}) = \frac{-2740}{T} + 9.965. \tag{2}$$

Equations (1) and (2) are valid in the temperatures between the melting and boiling points of the pure substances. Assuming Eq. (2) is valid to temperatures above the silicon melting point (1414 °C), the above equations give $p^{\circ}_{\mathrm{Si}} = 0.191$ Pa and $p^{\circ}_{\mathrm{P}} = 2.627 \times 10^{8}$ Pa at 1500 °C and $p^{\circ}_{\mathrm{Si}} = 0.789$ Pa and $p^{\circ}_{\mathrm{P}} = 3.177 \times 10^{8}$ Pa at 1600 °C which may indicate that the separation of phosphorus from liquid silicon can take place through vacuum treatment. However, since phosphorus concentration in silicon is low, the thermodynamic activity of phosphorus is much less than the silicon solvent, and therefore in vacuum refining both elements are simultaneously evaporated; however with different rates. A very useful kinetic criterion for evaluating the feasibility of removing a dilute solute element (P here) from a molten metal (Si here) is Ollete's volatility coefficient α for monatomic evaporation of the both elements [2]:

$$\alpha = \frac{\gamma^{\circ}_{\mathrm{P}}\, p^{\circ}_{\mathrm{P}}}{p^{\circ}_{\mathrm{Si}}} \left(\frac{M_{\mathrm{Si}}}{M_{\mathrm{P}}} \right)^{1/2}, \tag{3}$$

where $\gamma^{\circ}_{\mathrm{P}}$ is the Henrian activity coefficient of P in Si (silicon shows Raoultian behaviour) and M_{Si} and M_{P} are the atomic weight of Si and P, respectively. Parameter $\alpha > 1$ shows that the phosphorus is evaporated faster

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[*] **Corresponding author:** Jafar Safarian, Norwegian University of Science and Technology, Alfred Getz Vei 2, No-7491, Trondheim, Norway; E-mail: Jafar.Safarian@material.ntnu.no.

Received: July 4, 2011. Accepted: December 14, 2011.

than silicon, while $\alpha < 1$ shows higher rate of silicon than phosphorus and $\alpha = 1$ shows equal evaporation rates for both. The activity coefficient of phosphorus in silicon rich Si-P melts can be estimated as $\gamma_P^\circ \approx 0.522$ considering the reported data by Zaitsev et al. [3] for the low phosphorus containing silicon melts. Hence, we obtain $\alpha = 6.8 \times 10^8$ and 2.0×10^8 for 1500 °C and 1600 °C, respectively. Obviously, phosphorus can be eliminated from molten silicon through vacuum distillation.

The purification of metallurgical grade silicon (MG-Si) by vacuum treatment has been investigated through experimental works in the last two decades. Suzuki et al. [4] carried out silicon vacuum treatment at 1450 °C and 1550 °C in 0.027 Pa and observed phosphorus change from 32 ppmw to 6–7 ppmw within six hours. Ikeda and Maeda studied the purification of MG-Si with electron beam re-melting technique under 0.01 Pa [5]. They removed phosphorus from 15–30 ppmw to around 3 ppmw in relatively short times. Yuge et al. [6] used vacuum induction melting in 6.7 Pa at 1500 °C and they removed phosphorus down to below 0.2 ppmw from 5 ppmw within 10 hours. In another study [7], they carried out the vacuum induction melting of MG-Si at 1500 °C, 1550 °C and 1642 °C in 0.014–0.016 Pa and removed P below 0.1 ppmw at 1642 °C within 7 hours. It has also been indicated in pilot scale that phosphorus removal from MG-Si to low levels acceptable for photovoltaic applications is possible through vacuum treatment by electron beam gun [8]. The phosphorus evaporation from molten silicon in 0.001–0.01 Pa by electron beam irradiation in pilot scale has shown phosphorus removal from 25 ppmw to less than 0.1 ppmw in 1.2 hours [9]. Application of the same technique and under 5–7 Pa pressure indicated fast removal rate of P from 200 ppmw to about 1 ppmw [10]. The application of vacuum induction melting in lower pressures than 0.1 Pa and different temperatures up to 1600 °C has also shown phosphorus removal from 15 ppmw to below 1 ppmw within two hours [11]. A numerical simulation on the phosphorus removal from silicon in vacuum induction refining has been recently developed by Zheng et al. [12] and the effects of different parameters on phosphorus removal has been evaluated.

The vacuum refining of MG-Si using electron beam gun and induction melting has been studied through the previous works [4–12]. Although silicon content in MG-Si is around 99 wt%, the composition of the impurities varies with regard to the compositions of the raw materials used for silicon production. Moreover, the effect of many impurities exist in MG-Si on the thermodynamics properties of silicon is not known. Therefore, in the present study, the removal of phosphorus from silicon is studied, while no other impurity exists in the melt. This may clarify more details of the kinetic and mechanism of the phosphorus evaporation from pure liquid silicon.

2 Experimental procedure

Hyper-pure polycrystalline silicon was purchased and it was doped by phosphorus through the addition of red phosphorus to the molten silicon. Several analysis of the produced Si-P alloy indicated phosphorus concentration of 314.1 ± 7 ppmw in silicon. A mixture of 19.1 g of this alloy with 280.9 g of the pure original silicon was used for every individual experiment to maintain the initial mass of the melt as 300 g containing 20 ppmw phosphorus. The Si-P alloy was first charged into a graphite crucible with 64 mm inside diameter and 150 mm height and pure silicon particles on top.

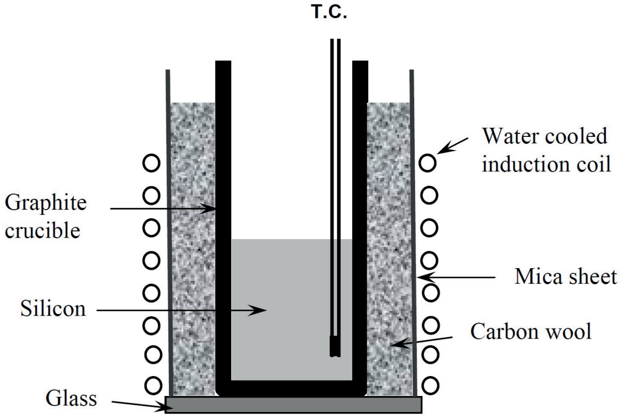

Figure 1. Schematic of the experimental set up.

The melting of Si-P alloy was done in an induction furnace, the experimental setup is schematically shown in Figure 1. The furnace chamber cleaned up from oxygen through two times evacuation and argon (+99.99%Ar) flashing. The melting was then done in 0.5 ± 0.2 Pa, while the melt temperature was measured by a thermocouple type C. It was experienced that melting step takes place between 8 to 10 minutes and then after melting completion the temperature rises quite fast. For instance, the temperature increase after melting to 1500 °C and 1600 °C takes less than a minute. Hence, in this short period the chemical composition is not significantly changed regarding the much longer refining times at constant temperatures. It was also observed that heat is more generated on the lower parts of the crucible so that Si-P alloy is melted at initial and then pure silicon particles. This was always observed through a top window above the crucible. The molten silicon was kept under vacuum at 1500 ± 5 °C and 1600 ± 5 °C for different durations. After refining the melt was casted in water cooled copper mould.

The solidified silicon was crushed down to a fine powder in a ring mill. Three samples from each experiment were taken with around 20–30 milligram mass for analysis. The chemical compositions were measured by high resolution inductively coupled plasma mass spectrometry (ICP-MS)

Refining time (min)	0	10	30	60	150	300
1500 °C	16.66 ± 0.9	15.45 ± 0.1	14.75 ± 0.8	13.28 ± 0.5	9.8 ± 1.1	–
1600 °C	16.66 ± 0.9	15.47 ± 0.5	14.0 ± 0.2	10.89 ± 0.6	5.86 ± 0.3	1.5 ± 0.3

Table 1. The measured phosphorus concentrations in refined silicon by ICP-MS. The numbers are averages over three samples in ppmw.

and the remained phosphorus in the refined silicon samples was determined.

3 Results

The measured phosphorus concentrations in the refined silicon samples for different durations are summarized in Table 1. The initial phosphorus concentration (16.66 ± 1 ppmw), which is obtained after complete melting, is less than the expected initial concentration of 20 ppmw. This is due to the partial evaporation of phosphorus within the melting step where the charged Si-P alloy is first melted and the melt volume is increased by the melting of the pure silicon particles. Hence, relatively fast phosphorus evaporation takes place from the initial melt pool due to the high initial concentration of phosphorus in the molten silicon which causes around 3 ppmw phosphorus loss.

According to the Table 1 data, the concentration of phosphorus in the melt decreases with vacuum refining time. This decrease is almost with a constant rate at 1500 °C so that the phosphorus concentration decreases from 16.7 ppmw to 13.3 ppmw in the first 1 hour at 1500 °C, and with 1.5 hour longer refining time it decreases to 9.8 ppmw. However, at 1600 °C the phosphorus evaporation is not linear and it is initially fast followed by a much slower rate. As we see, the concentration changes is from 16.7 ppmw to 5.9 ppmw in the first 2.5 hours and in twice the refining time it goes down to 1.5 ppmw.

4 Discussion

In order to understand the kinetics and so the involved mechanisms in the phosphorus evaporation from silicon, the obtained results are evaluated and discussed.

4.1 Reaction Order and Rate Constant

According to the kinetics principles, a general formula for the rate of phosphorus evaporation can be written as:

$$\text{Rate} = -\frac{dC}{dt} = k_{\mathrm{P}}\frac{A}{V}(C - C_e)^n, \tag{4}$$

where C is the concentration of phosphorus at time t, C_e is the equilibrium concentration of phosphorus, A is the melt surface and V is the melt volume. Parameter n is the order of reaction, and k_{P} is a proportionality factor referred to as *rate constant*. The latter parameter is a function of temperature T according to the Arrhenius equation:

$$k_{\mathrm{P}} = k_0 \exp\left(\frac{-Q_{\mathrm{app}}}{RT}\right), \tag{5}$$

where k_0 is a constant called frequency factor, and Q_{app} is the apparent activation energy for the phosphorus evaporation from the melt.

As mentioned in Section 1 phosphorus can be completely eliminated from the molten silicon due to very high α-value at the experimental temperatures. Thus, assuming $C_e \approx 0$ and re-arranging Eq. (4) for a first order reaction ($n = 1$), we obtain:

$$-\frac{dC}{C} = k_{\mathrm{P}}\frac{A}{V}dt. \tag{6}$$

Considering C_i as the initial phosphorus concentration, integration between the limits C_i at $t = 0$ and C at an arbitrary time t then gives:

$$\ln\left(\frac{C_i}{C}\right) = k_{\mathrm{P}}\frac{A}{V}t. \tag{7}$$

A plot of the $\ln(\frac{C_i}{C})$ versus the corresponding $\frac{A}{V}t$ value for the experimental data presented in Table 1 gives a linear relationship at both experimental temperatures as shown in Figure 2. This means that assuming a first order reaction is consistent for phosphorus evaporation under vacuum. It is worth noting that higher order reactions were also evaluated and they did not give better results than that obtained for the first order reaction. Hence, we conclude here that the phosphorus evaporation from liquid silicon takes place according to a first order reaction.

From the slop of the resulted lines in Figure 2, the rate constant $k_{\mathrm{P}} = 2.28 \times 10^{-6}$ m/s and $k_{\mathrm{P}} = 4.93 \times 10^{-6}$ m/s are obtained for 1500 °C and 1600 °C, respectively. These rate constants for the phosphorus removal are different from the reported rate constants for the phosphorus removal from MG-Si in 0.027 Pa by Suzuki et al. [4]. They reported rate constants 1.6×10^{-5} m/s and 2.0×10^{-5} m/s at 1450°C and 1550 °C, respectively. Their results are relatively close to the reported rate constants by Yuge et al. [7] through experiments in 0.014–0.036 Pa. Yuge and co-workers obtained rate constants 1.0×10^{-5} m/s, 2×10^{-5} m/s and

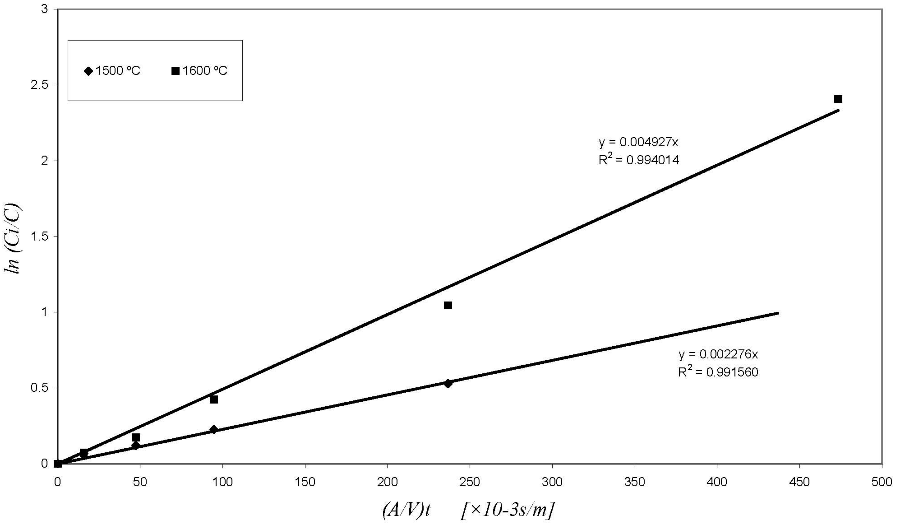

Figure 2. Relationship between $\ln(\frac{C_i}{C})$ and $\frac{A}{V}t$ for phosphorus removal at different temperatures.

2.2×10^{-5} m/s for 1450 °C, 1548 °C and 1642 °C, respectively. The recently reported rate constants for 1510 °C and pressures of 0.01, 0.1 and 1.0 Pa by Zheng et al. [11] are all approximately 2.0×10^{-6} m/s. This value is around 10 times smaller than the mentioned other works [4, 7]; however, it is closer to the results of the present study.

4.2 The Activation Energy of Phosphorus Evaporation

Compared to the studies done in higher vacuum conditions than the applied vacuum in the present study [4, 7], the rate constant of phosphorus evaporation is significantly dependent on temperature and it is almost doubled through the temperature change from 1500 °C to 1600 °C. The relationship between the rate constant for the phosphorus evaporation from pure liquid silicon and temperature under 0.5 Pa atmospheres may be presented as:

$$\ln k_{\mathrm{P}} = -\frac{25633}{T} + 1.4645. \tag{8}$$

Considering Eq. (5) and Eq. (8), the frequency *factor* $k_0 = 4.325$ m/s and an apparent activation energy $Q_{\mathrm{app}} = 213.1$ kJ/mol are obtained. This activation energy is larger than the calculated activation energy 130 kJ/mol by Yuge et al. [7]. However, it is smaller than the Si-P bond energy 288.71 kJ/mol [13] as we would expect, since silicon is in the liquid state. The obtained larger activation energy here than Yuge et al. [7] is related to the differences in the experimental conditions in the two studies.

4.3 Kinetics of Phosphorus Evaporation

The concentration changes of phosphorus with time at a given temperature can be calculated considering Eqs. (7) and (8):

$$C = C_i \exp\left(-4.325 \exp\left(\frac{-25633}{T}\right) \cdot \frac{A}{V} t\right). \tag{9}$$

Equation (9) can be used to study the effect of temperature; melt geometry and initial phosphorus concentration on the kinetics of phosphorus removal from silicon under intermediate vacuum refining conditions i.e. 0.5 Pa.

4.3.1 Refining Temperature

Figure 3 shows the calculated composition changes of phosphorus in silicon under the experimental conditions of this study for various temperatures. The calculated concentration changes are consistent with the experimental data at 1500 °C and 1600 °C and they predict the kinetics of phosphorus removal at other temperatures. The shape of the curves in Figure 3 is almost linear at low temperatures 1450 °C and 1500 °C and a curvature is appeared at higher temperatures.

4.3.2 Melt Geometry

The effect of melt geometry, which can be described by the changes in A/V ratio, can be studied using the calculated phosphorus concentration changes presented in Figure 4. For the experiments in this study we have $A/V = 26.3\ \mathrm{m}^{-1}$ and the calculated curves in Figure 4 are in different magnitudes of this ratio. As we see the kinetics of phosphorus removal increases with increasing A/V ratio and the extent of the initial rapid phosphorus removal increases extensively with increasing the melt surface area. This is due to similar effect of A/V ratio increase as k_{P} increase in Eq. (9).

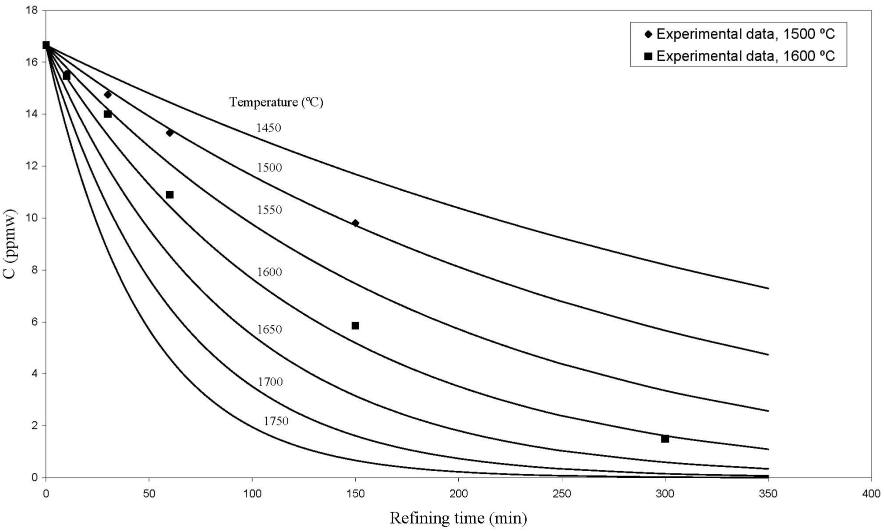

Figure 3. The changes of phosphorus concentration with refining time for different temperatures.

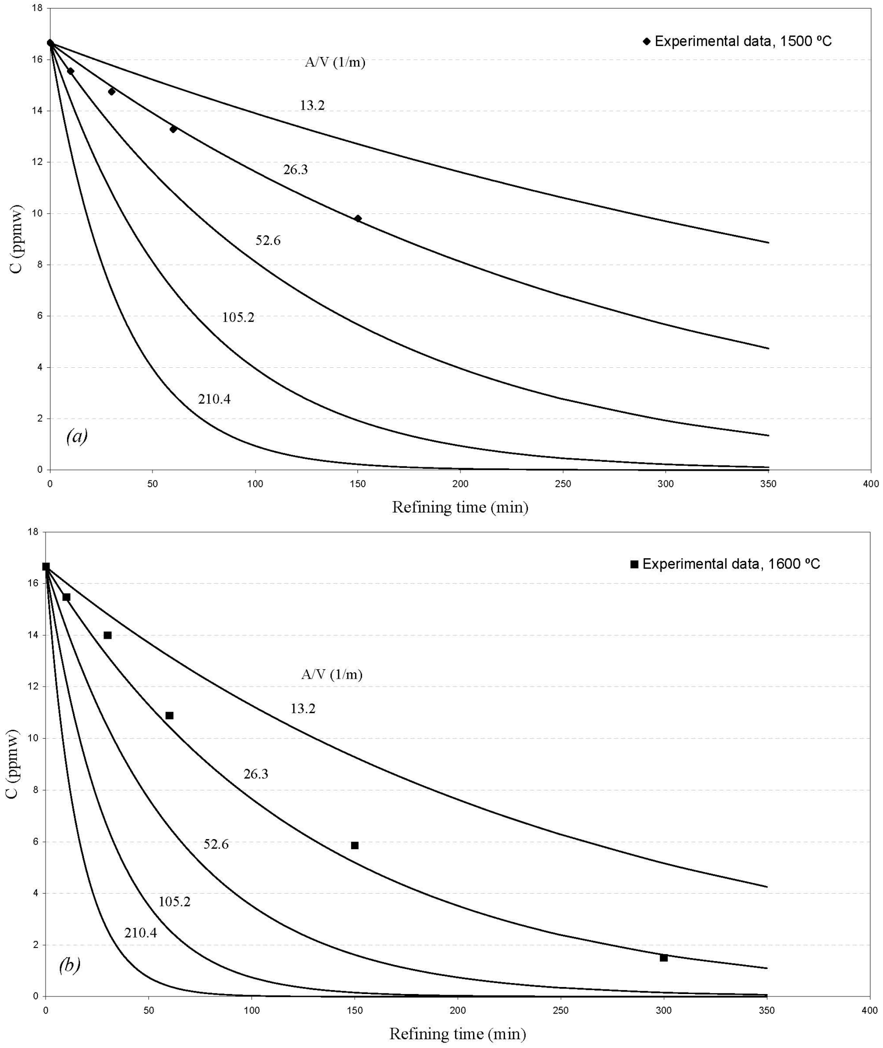

Figure 4. The changes of phosphorus concentration with refining time for different A/V ratios of the melt.

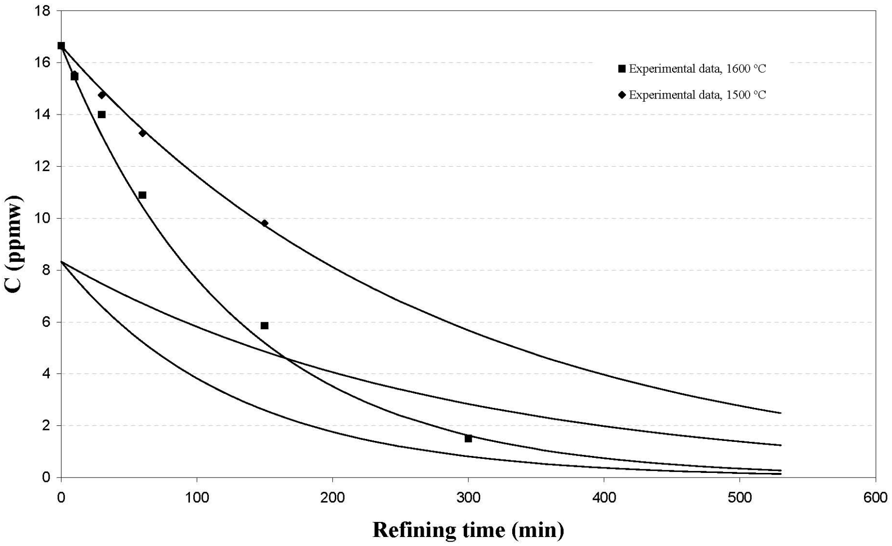

Figure 5. The changes of phosphorus concentration with refining time for different initial phosphorus concentrations.

Comparing the calculations for 1500 °C and 1600 °C it is observed that very fast phosphorus removal rates in vacuum induction refining is achievable with increasing both temperature and the A/V ratio.

4.3.3 Initial Phosphorus Concentration

The initial composition of the impurity is a parameter which may affect the selection of the raw material, which is used for the purification process due to its effect on the economy of the refining process. The effect of the initial phosphorus concentration on the phosphorus removal was calculated for the applied experimental conditions of the present study as illustrated in Figure 5. It is observed that the kinetics of phosphorus removal is affected by the initial phosphorus concentration and overall the extent of the fast initial phosphorus removal increases with increasing the initial phosphorus concentration. This is due to the larger driving force for the phosphorus evaporation reaction at higher concentrations. Figure 5 indicates that in order to gain phosphorus concentrations down to the levels acceptable for SoG-Si, for instance around 0.5 ppmw, longer refining times is required for higher initial phosphorus concentrations. For instance, Figure 5 shows that this level is reached at 1600 °C within 6 hours when the initial concentration is 8.33 ppmw. However, it is reached within 8 hours when the initial concentration is two times higher, 16.66 ppmw.

4.4 Approaching the Mechanism of Phosphorus Removal

Considering no concentration profiles in the bulk melt and gas phases, the removal of the dissolved phosphorus in molten silicon occurs through the following three steps:

1. Mass transport of phosphorus in a thin melt boundary layer adjacent to the surface.
2. Evaporation of phosphorus at the surface.
3. Gas phase mass transport of the phosphorus over the melt surface.

The above three steps are schematically shown in Figure 6. Considering k_m, k_c and k_g are the mass transport coefficients of phosphorus in these three steps, respectively, according to the mass transport principles we may write:

$$k_{\mathrm{P}} = \left(\frac{1}{k_m} + \frac{1}{k_c} + \frac{1}{k_g}\right)^{-1}. \tag{10}$$

The mass transport coefficients k_m, k_c and k_g are discussed in the following.

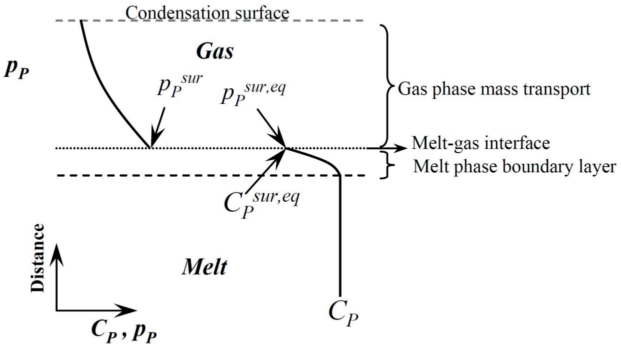

Figure 6. The mass transfer of phosphorus from silicon melt to the gas phase through a three step mixed control mechanism.

Experimental Temperature	Resistance to mass transfer (s/m)				Mass transfer coefficient (m/s)			
	$1/k_{\mathrm{P}}$	$1/k_m$	$1/k_c$	$1/k_g$	k_{P}	k_m	k_c	k_g
1500 °C	4.39×10^5	2.97×10^3	1.67×10^5	2.69×10^5	2.28×10^{-6}	3.36×10^{-4}	5.98×10^{-6}	3.71×10^{-6}
1600 °C	2.03×10^5	2.66×10^3	4.83×10^4	1.52×10^5	4.93×10^{-6}	3.75×10^{-4}	2.07×10^{-5}	6.58×10^{-6}

Table 2. The determined kinetic parameters for the mass transfer of phosphorus from the silicon melt to the gas phase.

4.4.1 Mass Transfer in the Melt Boundary Layer

Based on the developed model by Machlin [14], the mass transfer coefficient in the melt boundary layer can be calculated by Eq. (11):

$$k_m = \left(\frac{8D_{P,m}v_m}{\pi r}\right)^{1/2}, \tag{11}$$

where r is the melt radius, $D_{P,m}$ is the phosphorus diffusion coefficient in the melt and v_m is the melt surface velocity. The diffusion coefficient of phosphorus close to the silicon melting point has been determined as 2.3×10^{-8} m^2/s [15]. Considering the Stokes–Einstein Equation [16], where the diffusion coefficient is proportional with the temperature over the dynamic viscosity of the melt, and also the liquid silicon viscosity dependence on temperature [17], we may calculate the phosphorus diffusion coefficient above silicon melting point using the above known diffusion coefficient at the melting point. This gives $D_{P,m} = 2.55 \times 10^{-8}$ m^2/s and 3.17×10^{-8} m^2/s for 1500 °C and 1600 °C, respectively. The melt surface velocity v_m can be calculated through the calculating the characteristic velocity U_0 of the melt ($v_m = U_0 \cdot A$). Szekely et al. [18] developed an empirical formula to determine the characteristic velocity of the inductively stirred melts:

$$U_0 \cong J_0\sqrt{\frac{\sigma f}{\rho}\mu_0 L^2}, \tag{12}$$

where J_0 is the coil current, σ is the melt electrical conductivity, f is the characteristic frequency, ρ is the melt density, μ_0 is the magnetic permeability of the free space (1.2566×10^{-6} H/m) and L is the characteristic length (melt diameter). Considering $\sigma = 1.23 \times 10^6$ S/m [19], $\rho = 2.48$ kg/m^3 (1500 °C) and 2.46 kg/m^3 (1600 °C) [20] and the experimental and operational conditions, we obtain $v_m = 0.0557$ m/s and 0.0559 m/s for the 1500 °C and 1600 °C, respectively. As we see the melt surface velocity is relatively high so that with regard to the crucible diameter (0.064 m), the melt at the whole surface is renewed in around one second. It is worth noting that in some failed experiments with not proper vacuum sealing, solid particles such as silicon oxide and silicon nitride were formed on the melt surface. The rapid melt surface velocity is confirmed with observing fast movement of these particles on the melt. It is worth mentioning that Eq. (12) might be valid for the melts with no induction in the crucible. For the present study, the silicon melt is hold in the graphite crucible and the induction takes place also in the crucible and it may affect the calculations done by Eq. (12). The authors, however, has modeled the induction melting of silicon in the graphite crucible by Comsol multiphysics simulation software and the calculated velocities are close to the results of applying Eq. (12) for the melt surface velocities. The results of the modeling work will be published separately.

The mass transfer coefficient in the melt boundary layer can be calculated by the calculated $D_{\mathrm{P},m}$ and v_m values for the experimental temperatures as shown in Table 2. It is observed that the mass transfer coefficient in the melt is affected slightly by temperature change. On the other hand, the k_m values are much larger than the total k_{P} values and therefore we may conclude that the rate of vacuum phosphorus removal from silicon in vacuum induction refining is not controlled by the mass transport in the boundary later of the melt.

4.4.2 Phosphorus Evaporation

The rate of the evaporation of a substance at elevated temperatures can be calculated by the Hertz–Langmuir–Knudsen equation [21]. When a perfect vacuum is not used, i.e. the present study, the rate of solute element (P) evaporation from a melt (Si) per unit area can be expressed by this equation as [21]:

$$W = \eta\frac{p_{\mathrm{P}}^{\mathrm{sur,eq}} - p_{\mathrm{P}}^{\mathrm{sur}}}{\sqrt{2\pi \mathrm{RTM_P}}}, \tag{13}$$

where $p_{\mathrm{P}}^{\mathrm{sur,eq}}$ is the partial pressure of phosphorus in equilibrium with the dissolved phosphorus, and $p_{\mathrm{P}}^{\mathrm{sur}}$ is the partial pressure of phosphorus on the melt surface (Figure 6). Parameter η is called evaporation coefficient, which is attributed to the surface contamination. The value of η is smaller than unity; however for clean melts it reaches unity. Since in the present study the melt is highly pure, we may assume $\eta \approx 1$. Using Eq. (13) and mass balance, the rate constant of the monatomic evaporation of phosphorus can be calculated as [22]:

$$k_c = 4.43 \times 10^4\left(\frac{M_{\mathrm{P}}}{T}\right)^{1/2}\exp\left(\frac{\Delta G^\circ}{\mathrm{RT}}\right)/\rho, \tag{14}$$

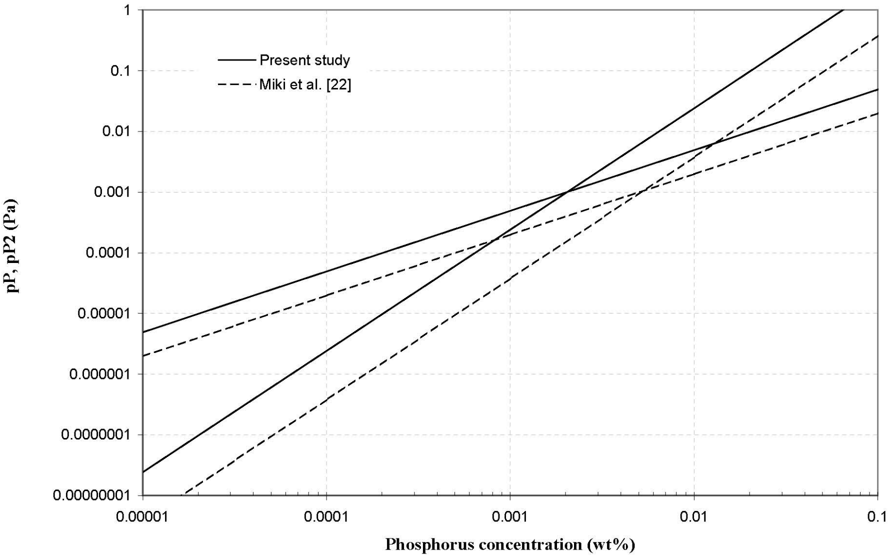

Figure 7. Relationship between the equilibrium partial pressure of P and P_2 gases and the dissolved phosphorus in silicon at 1550°C.

where ΔG° is the Gibbs energy changes in the phosphorus evaporation, which is here considered to be through monatomic evaporation at low concentrations:

$$\underline{\text{P}}(\text{wt\%}) = P(g) \quad \Delta G^\circ = 347\,500 - 88.86T \text{ J/mol.} \tag{15}$$

The above ΔG° relationship with temperature is obtained through the outlined method presented by Miki et al. (1996), however with considering the presented equilibrium between the dissolved phosphorus and diatomic phosphorus by Zaitsev et al. (2001):

$$\underline{\text{P}}(\text{wt\%}) = P_2(g) \quad \Delta G^\circ = 99\,500 - 29.46T \text{ J/mol.} \tag{16}$$

The relationship between the dissolved phosphorus concentration in silicon and the equilibrium partial pressure of phosphorus in Eq. (15) and also (16) is shown in Figure 7. It is observed that the monatomic phosphorus evaporation in concentrations less than 20 ppmw is more dominant than diatomic evaporation. This critical concentration is smaller than the suggested concentration as around 50 ppmw by Miki and co-workers, which is seen considering their represented data in Figure 7. Since the initial phosphorus concentration in the present study is less than 20 ppmw, we here consider monatomic evaporation through reaction (15) as the dominant chemical reaction.

Considering $\rho = 2.48\ \text{kg/m}^3$ (1500 °C) and $2.46\ \text{kg/m}^3$ (1600 °C) [21], k_c can be calculated as shown in Table 2. As seen, the rate of the chemical reaction is highly affected by temperature so that it is four times greater at 1600 °C than 1500°C. Comparing k_c values with the experimentally determined k_P values, we see that $k_\text{P} \approx 0.38k_c$ at 1500 °C and $k_\text{P} \approx 0.24k_c$ at 1600 °C. These results indicate that the removal of phosphorus in the intermediate pressures i.e. 0.5 Pa is more chemical reaction controlled at lower refining temperatures.

4.4.3 Mass Transfer in the Gas Phase

The calculation of the apparent mass transfer coefficient in the gas phase (k_g) is complicated due to the contribution of many unknown parameters. Zheng et al. [12] have recently developed a numerical approach for calculating this parameter, where the mass transfer coefficient of phosphorus in the gas phase is calculated considering the diffusivities of both Si and P in the gas phase. In the present study, however, the mass transfer resistance in the gas phase ($1/k_g$) is simply calculated by subtracting the determined mass transfer resistances $1/k_m$ and $1/k_c$ from the total mass transfer resistance $1/k_\text{P}$ as seen in Table 2. Comparison of the k_g values with the other mass transfer coefficients indicates that mass transfer to the gas phase is more rate limiting step at higher temperatures. The presented data in Table 2 indicate that under intermediate vacuum conditions the kinetics of phosphorus removal is controlled by both chemical evaporation on the melt surface and gas phase mass transfer and the latter one is more dominant at higher temperatures. This issue may indicate that the application of higher vacuum than 0.5 Pa increases the removal rate for the phosphorus to a considerably faster rate than what observed for 1600 °C.

5 Conclusions

The kinetics and mechanism of phosphorus removal from molten silicon was studied through vacuum induction refining in 0.5 Pa at 1500 °C and 1600 °C. The main conclusions can be summarized as:

1. Phosphorus removal from molten silicon occurs through a first order reaction with the rate constants $k_\mathrm{P} = 2.28 \times 10^{-6}$ m/s and $k_\mathrm{P} = 4.93 \times 10^{-6}$ m/s at 1500 °C and 1600 °C, respectively.

2. An apparent activation energy for phosphorus evaporation is obtained as $Q_\mathrm{app} = 213.1$ kJ/mol.

3. The mass transfer of phosphorus in the inductively stirred melts is large and it does not limit the kinetics of phosphorus removal.

4. The rate of phosphorus removal is mix-controlled by chemical reaction and gas phase mass transport. Under medium vacuum conditions the mass transport in the gas phase is more dominant at higher temperatures.

Acknowledgments

The authors acknowledge the project fund provided by the Norwegian Research Council through the BASIC project (191285/V30).

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