

VACUUM REMOVAL OF THE IMPURITIES FROM DIFFERENT SILICON MELTS

Jafar Safarian, Buhle Xakalashe and Merete Tangstad

Norwegian University of Science and Technology (NTNU), Alfred Getz Vei 2, No-7491, Trondheim, Norway

ABSTRACT: Since silicon is still the dominant material in photovoltaic devices and the market of PV applications is growing, the demand for silicon feedstock is expected to be high in the near future. Although attempts have been made to develop economic processes for solar-grade silicon (SoG-Si) production, Siemens process is still the main production method. This process has high cost and potential environmental pollution and therefore developing new routes for SoG-Si feedstock production is required. Regarding the initial silicon production in electric furnace, the most economic way for silicon purification may be its processing in the liquid state. Vacuum refining of molten silicon is a process that can be applied to remove volatile elements from liquid silicon. In the present study, the removal of impurities from different liquid silicon melts is studied by vacuum induction experiments at 1600 °C and under 1 Pa pressure. The vacuum removal of the solute impurities such as P, Al, Ca, and Mn are evaluated through the ICP-MS analysis of the refined silicon. In particular, the elimination of phosphorus, which is always a problematic element in SoG-Si production processes, is studied. It is indicated that the kinetics of the volatile elements removal is affected by the initial chemical composition of the silicon melt. In particular, phosphorus removal from Si-P and Si-Fe-P melts is higher than the melts containing more impurities such as Metallurgical Grade silicon (MG-Si).

Keywords: Impurities, metallurgical grade, silicon, vacuum, refining

1 INTRODUCTION

Vacuum distillation technique for the purification of molten metals and alloys has been developed mainly in the last century. This technique can be used to remove for example bismuth, arsenic and antimony from liquid copper [1] or copper and tin from melted scrap steel [2]. In secondary steelmaking, degassing and decarburization through vacuum refining techniques such as VD, VAD and VOD are widely used [3]. With regard to the rapid growth of SoG-Si production for PV industry, many techniques for economical purification of silicon have been studied in the recent years. Vacuum refining has also been applied in laboratory scale to remove particular impurities from silicon such as phosphorus.

The difference in the vapour pressures of the liquid metal components at elevated temperatures is the basic principle of crude metal vacuum distillation. The relationship between the saturated pressure and temperature for some pure elements is illustrated in Fig. 1. The curves in the figure have been calculated using the reported thermodynamic data on vapour pressures of pure substances [4]. As we see, the vapour pressure of many elements is higher than silicon in a wide temperature range, while a few elements such as B and Ti show lower vapour pressures. Thus, the removal of many elements from liquid silicon seems to be possible. Based on the Hertz-Langmuir-Knudsen equation for the evaporation of substances in vacuum, Olette [5] developed a kinetic volatility criterion for vacuum refining. This criterion for the monatomic evaporation of impurity i in dilute solution with silicon solvent can be written as:

$$\alpha = \frac{\gamma_i^{\circ} p_i^{\circ}}{p_{Si}^{\circ}} \left(\frac{M_{Si}}{M_i} \right)^{1/2} \quad (1)$$

where p_{Si}° and p_i° are the vapour pressures of pure silicon and impurity at a given temperature, and γ_i° is the Henrian activity coefficient of the impurity. M_{Si} and M_i are the atomic weight of silicon and impurity, respectively. The magnitude of α from one solute to another indicates relative rates of refining when

monatomic evaporation controls rate of refining. If $\alpha > 1$, the impurity can be removed almost completely from silicon. If $\alpha < 1$, the impurity cannot be removed and the silicon evaporation rate is greater than the impurity. Obviously, $\alpha = 1$ shows that both silicon and the impurity are evaporated with equal rates.

The application of vacuum induction melting for the purification of metallurgical grade silicon (MG-Si) has been investigated through several experimental works. Suzuki et al. [6] carried out silicon vacuum treatment at 1450 °C and 1550 °C in 0.027 Pa within various refining times and observed significant removal of P, Ca and Al. In particular, they observed phosphorus change from 32 ppmw to 6-7 ppmw within six hours. The effect of temperature was not significant on P removal rate. In contrast, the removal rate of both Ca and Al was increased with increasing temperature. Considering the first order chemical reaction for the evaporation of these elements, they calculated the rate constants for P, Ca and Al evaporation. They also suggested that the overall evaporation rate of P and Ca is controlled by the diffusion of these elements through liquid silicon to the liquid-gas interface. Yuge et al. [7] melted silicon in vacuum atmosphere of 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, they investigated the removal rate of P, Ca and Al from MG-Si through vacuum induction melting at 1500 °C, 1550 °C and 1642 °C in 0.014-0.016 Pa using 0.04 kg silicon [8]. Considering their results, it is again found that temperature effect on the evaporation rate of phosphorus is less than that on Al and Ca evaporation rates. They could remove P and Ca under 0.1 ppmw at 1642 °C within 7 hours. They also did some silicon refinement under low pressure conditions between 4 and 190 Pa at 1460 °C and 1550 °C using 5 kg silicon. They observed that phosphorus removal under these conditions is slower and phosphorus can be removed to below 1 ppmw within 17 hours. Considering the first order removal rates for the elements they calculated the rate constants for P, Ca and Al removal as functions of temperature. Furthermore, they estimated the activation energies for their removal and obtained 130kJ/mol for phosphorus and 186 kJ/mol

for aluminium and 147 kJ/mol for calcium. Yuge and co-workers demonstrated that the overall rate of the removal of these elements is controlled by the diffusion in molten silicon and evaporation from the silicon surface. The kinetics of phosphorus removal from MG-Si has also been recently studied by Zheng et al. [9] and they indicated relatively high phosphorus removal rates from molten silicon through vacuum induction melting. It was indicated in our previous publication that many elements can be removed from MG-Si through vacuum refining [10].

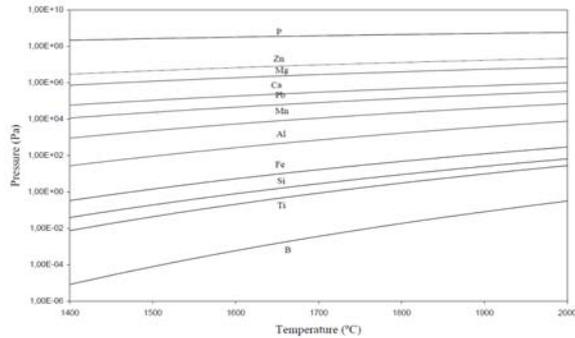


Figure 1: The changes of the standard vapour pressure of pure substances with temperature calculated from the reported thermodynamic data.

In the present study different silicon melts are refined using vacuum induction melting technique and the removal rates of the impurities are evaluated. In particular, the elimination of phosphorus, which is a problematic element in the processes applied for SoG-Si production, is studied.

2 EXPERIMENTAL PROCEDURE

Four different impure silicon materials were used in the present study. Electronic grade silicon (EG-Si) doped by phosphorus, EG-Si doped by both iron and phosphorus, an industrial MG-Si, and an industrial double leached MG-Si. We call these silicon materials here as A, B, C and D, respectively, and the measured chemical compositions of them by High Resolution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are shown in Table I.

Table I: The chemical composition of silicon materials in ppmw.

Vacuum melting experiments were carried out in a vacuum induction furnace under 0.5 Pa pressure. The

Silicon	B	Ca	Al	P	Ti	Mn	Fe
A	-	-	-	16.66 ±1.0	-	-	-
B	-	-	-	15.0 ±0.65	-	-	4938 ±350
C	68.79 ±3.0	970.6 ±27	2619 ±16	17.58 ±0.94	205.4 ±1.8	60.13 ±5.7	4675 ±91.6
D	21.87 ±0.4	144.4 ±5.7	880.2 ±31	24.24 ±1.2	16.81 ±0.55	2.01 ±0.14	298.2 ±11.1

experimental set up is schematically shown in Fig. 2. For each individual run 300 g silicon was melted in a graphite crucible with 64 mm inside diameter and 150 mm height. The graphite crucibles were machined from a dense graphite rod which shows not significant infiltration of molten silicon. The experiments were done at 1600 °C for

one hour and a rapid heating from the room temperature to the experimental temperature was applied. The heating from the silicon melting point (1414 °C) to 1600 °C was always less than 30 seconds, which is negligible compare to the holding times at this temperature. The temperature of the silicon melt was measured by a thermocouple type C located inside the melt with 10 mm distance from the crucible bottom and wall.

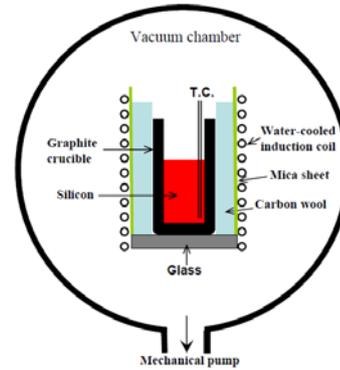


Figure 2: Schematic of the vacuum induction furnace and the experimental set up.

After vacuum refining, the melt was casted in a water cooled copper mold in order to rapidly solidify silicon with minimum segregation of the solute element. Silicon was then milled to a very fine powder in a disc mill. Three samples from each melt were then analyzed by ICP-MS and the averages were determined.

3 RESULTS AND DISCUSSION

The obtained results are presented and discussed as follows.

3.1 Composition changes through vacuum treatment

The measured chemical compositions of the refined silicon materials are presented in Table II. Comparing the initial composition of the silicon samples before and after refining indicates that there is no significant changes in the compositions of B, Fe and Ti, which are considered as not volatile elements in silicon regarding their low vapour pressures (Fig. 1). Both Fe and Ti show large negative deviations from the ideal solution and the values of γ_{Fe}^o and γ_{Ti}^o are quite small [11]. Therefore, the α -value for these elements is smaller than unity and their removal is not expected. Although small positive deviation from the ideal solution is observed for B in molten silicon [12], α -value smaller than unity is expected for B with regard to its much smaller vapour pressure than silicon (Fig. 1).

Table II: The chemical composition of the vacuum treated silicon materials in ppmw.

Silicon	B	Ca	Al	P	Ti	Mn	Fe
A-refined	-	-	-	10.89 ±0.57	-	-	-
B-refined	-	-	-	8.71 ±0.21	-	-	4987 ±164
C-refined	71.77 ±0.7	671.2 ±44	2033 ±45	12.36 ±1.2	210.1 ±4.3	41.1 ±1.1	4656 ±105
D-refined	23.14 ±0.8	129.5 ±7.3	823.2 ±27	18.82 ±0.8	17.29 ±0.76	1.46 ±0.06	294.3 ±9.4

The chemical composition data in Tables I and II show that Ca, Al, P and Mn are evaporated from molten

silicon by vacuum treatment. This is due to the higher vapour pressure of these elements than silicon so that they give greater α -values than unity. It is worth noting that P shows intermediate negative deviation from the ideal solution in its dilute solution [13]. Solute Al shows similar behaviour, whereas Ca and Mn show relatively large negative deviations from the ideal solution [14].

The evaporation fraction, which is the difference between the initial concentration of the impurity (C_i) and the concentration after one hour refining (C_{ref}), is shown in Fig. 3 for Ca, Al, P and Mn. This fraction is calculated by Eq. (2):

$$F = \frac{C_i - C_{ref}}{C_i} \times 100 \quad (2)$$

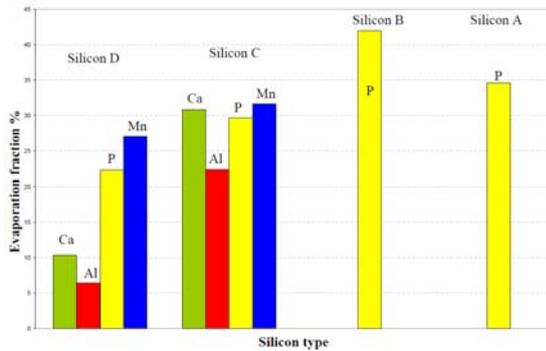


Figure 3: The evaporation fraction of the volatile elements from the silicon melts at 1600 °C and 0.5 Pa with one hour.

The information in Fig. 3 indicates that the evaporation of the volatile elements is affected by the initial chemical compositions of the melts. It is observed that the evaporation fraction is larger for the melts containing higher amounts of the impurities. This may be due to the larger driving force for the evaporation chemical reaction. The initial concentrations of Ca, Al and Mn in Silicon C are higher than silicon D, and therefore more evaporation of these elements are observed. The initial concentration of phosphorus in the silicon melts are close and the observed different evaporation fractions for phosphorus are not related to the initial phosphorus concentration so that for Silicon D with higher initial phosphorus concentration, the smallest evaporation is observed. It is observed that phosphorus evaporation from cleaner silicon melts A and B is higher than that from silicon melts C and D, which are in low purity.

3.3 Evaporation kinetics of the impurities

The evaporation of Al, Ca, Mn and P from molten silicon has been shown to take place according to a first order chemical reaction [6, 8]. Thus, based on the kinetics principles, the kinetics of evaporation of solute element i from the melt can be explained by Eq. (3) [10]:

$$\ln\left(\frac{C_i - C_f}{C - C_f}\right) = k_i \left(\frac{A}{V}\right)t \quad (3)$$

where k_i is the mass transfer coefficient of the impurity, A/V is the ratio of the melt surface over its volume, C is the concentration at the refining time t , and C_f is the final concentration of the impurity at infinite time. Since the

evaporation of Al, Ca, P and Mn to very low concentrations is possible regarding Eq. (1), it is a fair approximation to consider $C_f \approx 0$. Thus, we may calculate the rate constant with re-arranging Eq. (3):

$$k_i = \frac{\ln(C_i / C)}{(A/V)t} \quad (4)$$

Considering the melt geometry ($A/V=26.3 \text{ m}^{-1}$) and the concentrations of the impurities in the melt before and after refining, the rate constant for the evaporation of Al, Ca, P and Mn were calculated as summarized in Table III. The obtained mass transfer coefficients for Ca are significantly smaller than the reported values of $k_{Ca}=1.4 \times 10^{-5} \text{ m/s}$ and $k_{Ca}=1.7 \times 10^{-5} \text{ m/s}$ by Suzuki et al. [6] for Ca removal from MG-Si in 0.027 Pa at 1450 °C and 1550 °C, respectively. The determined Ca evaporation rate constants by Yuge et al. [8] in the temperature range of 1450-1642 °C and pressures within 0.008-0.036 Pa are in the range of $k_{Ca}=9 \times 10^{-6}$ to 5×10^{-5} , which are relatively close to the reported rate constants by Suzuki and co-workers. Comparing their results with the obtained k_{Ca} values in the present study may indicate that the evaporation of Ca from silicon is very dependent on the pressure and less temperature dependent. Similarly, the determined mass transfer coefficients for Al in this study are much smaller than the reported values of $k_{Al}=1.0 \times 10^{-5} \text{ m/s}$ and $k_{Al}=1.5 \times 10^{-5} \text{ m/s}$ by Suzuki et al. [6] for Al removal from MG-Si in 0.027 Pa at 1450 °C and 1550 °C, respectively. Yuge et al. [8] reported $k_{Al}=3.0 \times 10^{-6} \text{ m/s}$ to $1.5 \times 10^{-5} \text{ m/s}$ for vacuum refining of MG-Si in 0.014-0.036 Pa in the temperature range of 1450-1642 °C. Comparing these data with the calculated k_{Al} in this study it can be concluded again that Al evaporation kinetics is significantly affected by the pressure.

Table III: The calculated rate constants for the evaporation of Ca, Al, P and Mn from silicon melts at 1600 °C and 0.5 Pa.

Silicon	k_{Ca} (m/s)	k_{Al} (m/s)	k_P (m/s)	k_{Mn} (m/s)
A-refined	-	-	4.47×10^{-6}	-
B-refined	-	-	5.75×10^{-6}	-
C-refined	3.9×10^{-6}	2.68×10^{-6}	3.72×10^{-6}	4.0×10^{-6}
D-refined	1.15×10^{-6}	7.1×10^{-7}	2.67×10^{-6}	3.34×10^{-6}

The rate constants for the phosphorus evaporation for silicon melts C and D in Table III are smaller than the rate constants determined for vacuum treatment of MG-Si in other studies. Suzuki et al. [6] reported $k_P=1.6 \times 10^{-5} \text{ m/s}$ and $k_P=2 \times 10^{-5} \text{ m/s}$ for refining in 0.027 Pa at 1450 °C and 1550 °C, respectively. Moreover, $k_P=8 \times 10^{-6} \text{ m/s}$ to $2 \times 10^{-5} \text{ m/s}$ has been determined by Yuge et al. [8] in 0.014-0.036 Pa in the temperature range of 1450-1642 °C. Their higher rate constants than the calculated rate constants in the present study are expected with regard to the same effect of pressure on Ca and Al rate constants as mentioned above. Yuge and co-workers obtained, $k_P \approx 9 \times 10^{-7} \text{ m/s}$, and $4 \times 10^{-6} \text{ m/s}$ for MG-Si refining in 4-5.3 Pa and 190 Pa, respectively, with observing not much temperature effect. The determined rate constants for the silicon melts C and D in this study are a little larger than their results at higher pressures and lower than their results at lower pressures.

The little larger rate constant for the P evaporation from silicon B than silicon A is hard to explain. This

difference may be due to the thermodynamic activity of phosphorus in the silicon melt where the activity is slightly increased through the introduction of small amounts of Fe to the molten silicon containing low P concentrations [15]. The reported rate constants for P evaporation from high purity silicon such as silicon melts A and B in the presents study are around two times larger than the obtained values by Zheng et al. [9] as $k_p \approx 2 \times 10^{-6}$ m/s for vacuum refining at 1510°C and pressures between 0.01 Pa and 1 Pa. This difference may be due to the application of higher temperature in the present study.

The magnitude of the rate constant is very important in practice and it affects the vacuum refining process and its economy significantly. In order to show this importance the changes in the phosphorus concentration over the initial concentration (C/C_i) for the silicon melts A to D versus the refining time were calculated and the obtained results are plotted in Fig. 4. Assuming $C_p = 0.1$ ppmw as the required concentration for the solar grade silicon production, the vacuum refining times for the refining of silicon A and B are around half of the required times for refining silicon D.

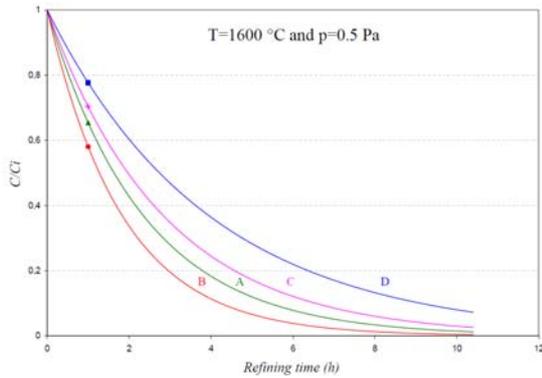


Figure 4: The phosphorus concentration changes in different silicon melts in the applied vacuum refining conditions of this study. Symbols: Experimental data.

3.4 Silicon yield

In the vacuum refining process, the silicon solvent is simultaneously evaporated with the evaporation of the solute impurities. This silicon loss can be calculated with regard to the no volatile elements such as Fe, B and Ti. Among these B and Ti are more reliable with regard to their smaller vapour pressures than silicon (Fig. 1). The remained silicon and the evaporated silicon from the melts C and D by mass balance were calculated considering B and Ti as the stable elements and the results are shown in Table IV.

Table IV: The calculated remained silicon and evaporated silicon with considering B and Ti for mass balance calculation.

Silicon melt	B as stable element		Ti as stable element	
	Remained silicon, g	Evaporated silicon, g	Remained silicon, g	Evaporated silicon, g
C	287.2	12.8	292.9	7.1
D	283.5	16.5	291.6	8.4

It is observed that silicon loss from the melt D is more than that from melt C which can indicate that the silicon evaporation kinetics is minimally affected by the type of original silicon. On the other hand, more silicon loss is observed when B is considered as the stable

element in the melt. This may show that considering boron is more reliable for the mass balance calculations. The silicon yields for the vacuum refining of melts C and D are therefore 95.7 % and 94.5 %, respectively.

4 CONCLUSIONS

The vacuum refining of four different silicon melts was investigated at 1600 and 0.5 Pa. It was observed that the kinetics of volatile elements evaporation from the melts is dependent on the melt chemical composition. In particular the rate of phosphorus removal from cleaner silicon melts is higher than MG-Si. The obtained results and their comparison with the literature data indicate that the rate of evaporation from molten silicon is more pressure dependent and less affected by temperature. Moreover, it was found that the silicon loss in the vacuum refining is slightly affected by melt composition.

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