

## A MATHEMATICAL MODEL FOR DISTRIBUTION OF CALCIUM IN SILICON BY VACUUM DIRECTIONAL SOLIDIFICATION

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### Abstract

Calcium is one of the main impurity elements in silicon. The removal of calcium strongly affects the quality of the polycrystalline silicon ingot produced by a vacuum directional solidification method. Based on the considerations of the theory of segregation, mass transfer and evaporation during vacuum directional solidification process, a mathematical model for calcium distribution in silicon was proposed and it can be used to explain the removal mechanism. In order to confirm the mathematical model, an industrial scale experiment on upgraded metallurgical grade silicon (UMG-Si) with an initial purity of 99.98 wt. % was performed. Since the reaction temperature strongly influences both the evaporation and segregation of calcium, the dependences of effective segregation coefficient ( $k_{eff}$ ) and the evaporation coefficient ( $k_E$ ) on temperature were carefully investigated. The results showed that the proposed mathematical model was highly consistent with the experimental data and the calcium removal efficiency mainly relied on the evaporation step.

**Keywords:** Vacuum directional solidification; Evaporation; Silicon melts; Calcium; Mathematical model

### 1. Introduction

Presently, the market demand for solar grade silicon (SOG-Si) has been growing rapidly [1]. Based on the requirements of the SOG-Si, the maximum content for calcium, which greatly affects the photoelectric conversion efficiency of the polycrystalline silicon cells, must be lower than  $1 \times 10^{-6}$  [2]. For this reason, many efforts have been made to remove calcium from silicon [3-5]. Plenty of studies have shown that both incineration processes and hydrometallurgical approaches, including slag refining [6-8], acid leaching [9], directional solidification [10] and vacuum refining [11], can be used to remove calcium.

Vacuum directional solidification furnace is mainly used for the polycrystalline silicon ingot production. Vacuum directional solidification process is an ideal technology for the removal of calcium from silicon, because the segregation coefficient of calcium is far lower than 1.0 [12] and the saturated vapor pressure of calcium is higher than silicon [13]. In this process, both the directional solidification segregation

and vacuum evaporation will affect the removal efficiency of calcium [14]. Thus, it is very valuable to research the combined effect of directional solidification segregation and vacuum evaporation during silicon purifying process by vacuum directional solidification furnace.

In the present study, a mathematical model for distribution of calcium by vacuum directional solidification with consideration of both the segregation effect and evaporation effect was proposed. The dependences of effective segregation coefficient ( $k_{eff}$ ) and the evaporation coefficient ( $k_E$ ) on the reaction temperature were carefully investigated. Finally, the mathematical model was confirmed through an industrial scale experiment.

### 2. Theoretical analyses

The thermodynamic analysis by Morita [15] and Miki [16] have shown that the removal of calcium from molten silicon is feasible. According to Shi [17], a mechanism with more industrial significance has been proposed as shown in Fig. 1. The removal of

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calcium can be summarized by the following five steps based on the segregation and evaporation mechanism during vacuum directional solidification melting.

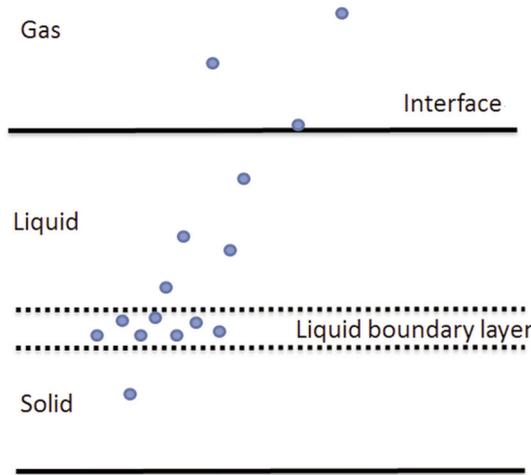


Figure 1. Schematic of the transport of calcium atoms

Step 1: calcium atoms segregated at the solid-liquid interface from solid phase to silicon melt;

Step 2: calcium atoms transferred across a liquid boundary layer from solid-liquid interface into liquid phase;

Step 3: calcium atoms transferred across a liquid phase;

Step 4: calcium atoms evaporated from the free melt surface into the gas phase;

Step 5: calcium atoms together with the gas in the chamber were removed by pump.

In order to study further describe the distribution of calcium in silicon, several simplifications are made as follows. (1) Calcium is assumed as the only impurity element in silicon and silicon feedstock is the single source of that in silicon; (2) No diffusion occurs in solid phases once they are formed ( $D_s = 0$ ); (3) Infinitely fast diffusion occurs in the liquid at all temperatures by virtue of a high diffusion coefficient ( $D_s = \infty$ ); (4) Solidus and liquids lines are straight segments; (5) The rate of solidification is equal to that of pull-down.

**2.1 The segregation of calcium in the solid-liquid interface**

In the process, calcium atoms are segregated in the solid-liquid interface because of the concentration difference. The amount of calcium that transfers from solid phase to liquid phase in the time of  $t$  can be expressed by:

$$\Delta C_s = (C_l - C_s) \tag{1}$$

where  $C_l$  is the content of calcium in the solid-

liquid interface,  $C_s$  is the content of calcium in solid phase. The segregation coefficient of calcium,  $k_0$ , can be express as follows [18]

$$k_0 = \frac{C_s}{C_l} \tag{2}$$

In fact, the effective segregation coefficient of calcium,  $k_{eff}$ , is more accurate than  $k_0$ , which can be written as [19]

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0) \text{EXP}(-\frac{v\delta}{D})} \tag{3}$$

where  $k_0$  is the segregation coefficient of calcium and calculated as  $8.0 \times 10^{-3}$  [20],  $v$  is solidification rate ( $\text{m} \cdot \text{s}^{-1}$ ), and  $\delta$  is the thickness of boundary layer (m).

**2.2 The transportation of calcium in a liquid phase**

Calcium transfers across a liquid phase from solid-liquid interface to melt interface in a short period of time as shown in Fig. 2.

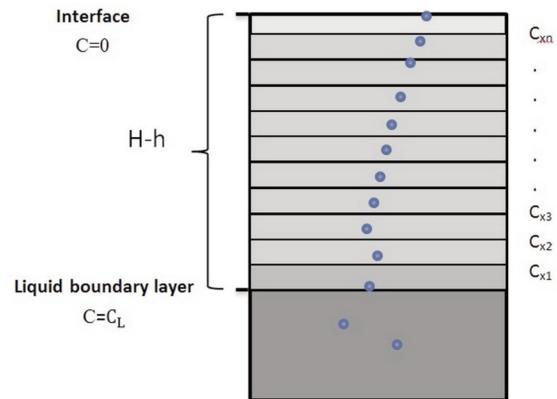


Figure 2. Schematic of the transport of calcium across a liquid phase

From Fig. 2, during the solidification process, while the calcium atom was transferring in boundary layer, the boundary layer was moving at the same time. Thus, the content of calcium in this process can be expressed, respectively:

$$\begin{cases} dC_1 = -k_D (C_l - C_{x1}) \frac{A}{V} dt \\ dC_2 = -k_D (C_{x1} - C_{x2}) \frac{A}{V} dt \\ dC_3 = -k_D (C_{x2} - C_{x3}) \frac{A}{V} dt \\ \dots\dots\dots \\ dC_n = -k_D (C_{xn} - 0) \frac{A}{V} dt \end{cases} \tag{4}$$



The content of calcium transfers across a liquid phase from solid-liquid interface to melt interface within a short period of time by calculating the integral is given by

$$C_z = -k_D \frac{(H-h)}{H} C_l \quad (5)$$

where  $H$  is the height of silicon ingot,  $h$  is the height of solidification,  $k_D$  is the mass transfer coefficient of calcium in liquid boundary layer. According to the two-film mass transfer model, the mass transfer coefficient of calcium in liquid boundary layer can be expressed as

$$k_D = \frac{D}{\delta} \quad (6)$$

where  $D$  is the calcium diffusion coefficient in molten silicon ( $\text{m}^2 \cdot \text{s}^{-1}$ ), it can be roughly estimated by Stokes-Einstein equation [21] modified by considering the effects of unequal mass of molecular silicon and calcium:

$$D = \frac{k_B T}{4\pi\mu_{Si} r_{Ca}} \left( \frac{M_{Ca} + M_{Si}}{2M_{Ca}} \right)^{1/2} \quad (7)$$

in which  $k_B$  is Boltzmann constant ( $\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$ ),  $T$  is melting temperature (K),  $r_{Ca}$  is atomic radius of calcium (m),  $\mu_{Si}$  is the viscosity of molten silicon ( $\text{Pa} \cdot \text{s}$ ) and can be described as follow according to literature [22].

$$\log \mu_{Si} (\text{mPa} \cdot \text{s}) = -0.727 + \frac{819}{T} \quad (8)$$

### 2.3 The evaporation of calcium from the melt surface

In the process of evaporation, the content of calcium within a short period of time can be expressed as

$$dC = -k_E C_z \frac{A}{V} dt \quad (9)$$

with

$$k_E = \frac{P_{Ca}^* \gamma_{Ca} M_{Si}}{\rho_{Si} \sqrt{2\pi RT M_{Ca}}} \quad (10)$$

in which  $M_{Ca}$  is the molar mass of calcium ( $\text{kg} \cdot \text{mol}^{-1}$ ),  $R$  is the ideal gas constant ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $P_{Ca}^*$  is the vapor pressure of pure calcium (Pa),  $\rho_{Si}$  is the molar density of silicon melt ( $\text{mol} \cdot \text{m}^{-3}$ ),  $M_{Si}$  is the

molar mass of silicon ( $\text{kg} \cdot \text{mol}^{-1}$ ),  $\gamma_{Ca}$  is the activity coefficient of calcium. According to thermodynamic properties of calcium in silicon reported by Miki et al [23], it was calculated as follows

$$\log \gamma_{Ca(l)} = 1.53 - \frac{7670}{T} \quad (1723 \sim 1823 \text{ K}) \quad (11)$$

Inserting Eq. (10) in (9), yields

$$dC = k_D k_E \frac{(H-h)}{H^2} C_l dt \quad (12)$$

From Eq. (12), we find the relationship between the content of calcium by evaporation and time. Thus, in the process of evaporation, the amount of calcium that evaporates from the free melt surface in the time of  $t$  can be expressed as

$$\Delta C_g = k_D k_E \frac{(H-h)}{H^2} C_l \quad (13)$$

### 2.4 The overall transportation of calcium

The calcium segregation in the solid-liquid interface and the evaporation on the melt surface should take place simultaneously, which causes the variation of the calcium content in the liquid phase at any time. However, according to the law of conservation of mass, the content of calcium in the liquid phase in a short period of time can be expressed as:

$$\Delta C = \Delta C_s - \Delta C_g \quad (14)$$

Substituting Eqs. (1) and (13) into Eq. (14),

$$\frac{d\Delta C}{dt} = \left( C_l - C_s - k_D k_E \frac{(H-h)}{H^2} C_l \right) \quad (15)$$

After a period of directional solidification, the content of calcium in melt can be written as

$$C_s = k_{eff} C_0 (1-X)^{k_{eff}-1} \exp\left(-k_D k_E \frac{X}{H}\right) \quad (16)$$

here,  $X$  is solidification fraction ( $X = v t/H$ ). The general Eq. (16) describes a mathematical model for distribution of calcium in silicon by vacuum directional solidification. This Eq. (16) includes two items:  $k_{eff} C_0 (1-X)^{k_{eff}-1}$  is Scheil's equation, which stands for the effect of directional solidification; and  $\exp\left(-k_D k_E \frac{X}{H}\right)$  is the influence of transfer and evaporation.



### 3. Experimental

Experiments were conducted in an industrial vacuum directional solidification furnace. Fig. 3 shows the schematic view of the experimental apparatus, which consists of vacuum system, melting system and pulling system. TC1 and TC2 are two thermocouples measuring the temperature of the silicon ingot at the top and bottom respectively.

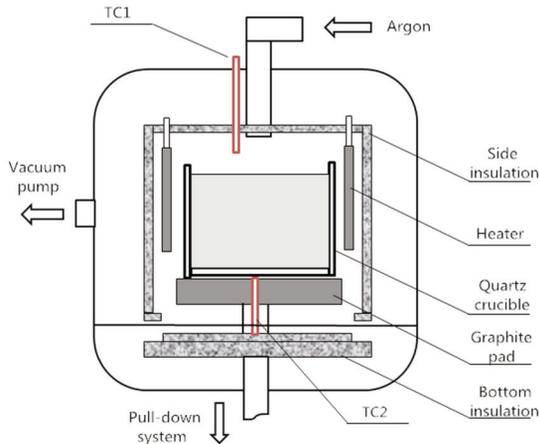


Figure 3. Schematic of experimental apparatus

UMG-Si powder with an initial purity of 99.98 wt. % was used in the experiment. The initial content of Ca was  $3.6533 \times 10^{-4}$  wt. %. Before being processed by refining, 500 kg UMG-Si was placed in the square quartz crucibles of a size  $840 \times 840 \times 480$  mm<sup>3</sup>, with Si<sub>3</sub>N<sub>4</sub> coating. In order to prevent the silicon from attaching to the heater and heat insulation to damage them, a layer of silicon briquette was covered on the silicon powder surface. And then the heating was turned on until the pressure of chamber was pumped below 0.1 Pa. After the silicon ingot was absolutely melted, held the temperature of TC1 at 1823 K for 1 hour and then pulled the crucible down at the rate of  $2.5 \mu\text{m} \cdot \text{s}^{-1}$ .

Finally, the cooled silicon ingot was cut along the growth direction by the diamond saws cutting machine and the diamond wire cutting machine. Six samples were chosen in the central region from the bottom to the top, as shown in Fig. 4.

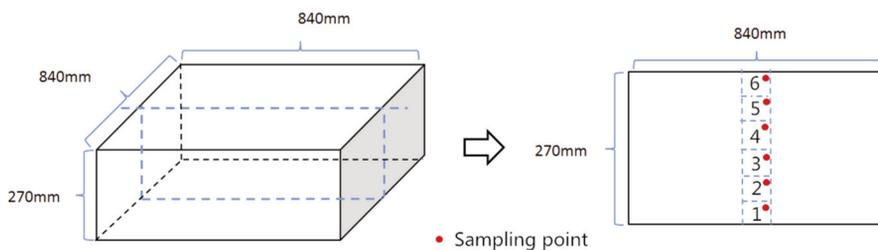


Figure 4. Sampling schematic diagram of experimental

The impurity contents before and after refining were analyzed by glow discharge mass spectrometry (GD-MS).

### 4. Results and discussion

#### 4.1 Mathematical model validation

The contents of calcium in silicon ingot after vacuum directional solidification at different heights are shown in Fig. 5.

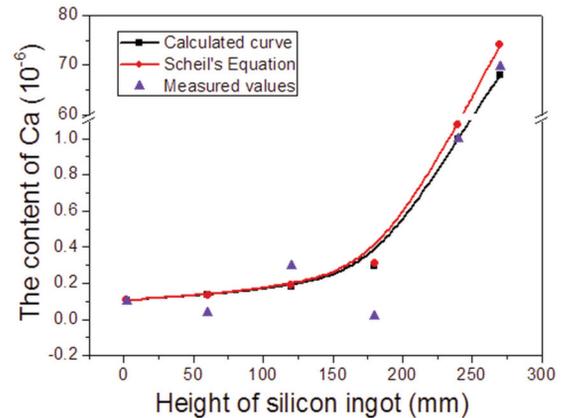


Figure 5. The contents of calcium at different heights ( $10^{-6}$ )

As shown in Fig. 5, it is clear that the concentration of calcium increased from bottom to the top of the ingot, and the content of calcium in the top of the silicon ingot is far higher than that in the bottom and middle of the silicon ingot. This is because the segregation coefficient of calcium is far less than 1 and calcium can be enriched in liquid phase. Those two curves obtained by our calculation and from the Scheil's equation. Based on the comparison between then, the calculated curve overlaps basically that from Scheil's equation in the middle to lower part of silicon ingot can be found, but there is difference between two curves in the upper part of silicon ingot as well. Furthermore, the measured value is much closer to the calculated curve than the curve by Scheil's equation as the height of silicon ingot rises. This is due to that calcium was evaporated from the free melt surface at any time during the solidification process. In the early, the evaporation was too weak to affect the segregation. When the evaporation was so enough that

the concentration gradient of calcium in the melt was affected, the segregation was also affected by evaporated finally.

It should be highlighted that the theoretical results obtained from Eq. (16) agreed well with the experimental curve, especially for the experimental data of the top part of the silicon ingot. This indicates that the mathematical model for distribution of calcium in silicon by vacuum directional solidification is credible. There are some reasons to believe that directional solidification segregation and vacuum evaporation both influenced the removal of calcium in silicon during silicon purifying process by vacuum directional solidification.

#### 4.2 $k_{eff}$ and $k_E$ at the different temperature

Temperature is the one of most important melting parameters which strongly affects the removal efficiency of calcium. This is because temperature affects both the segregation and the evaporation during vacuum directional solidification. In this case,  $k_{eff}$  and  $k_E$  at different temperatures from 1650 K to 1900 K were calculated, as plotted in Fig. 6.

From Fig. 6,  $k_E$  increases with the temperature. It is well known that, for a reaction about evaporation in

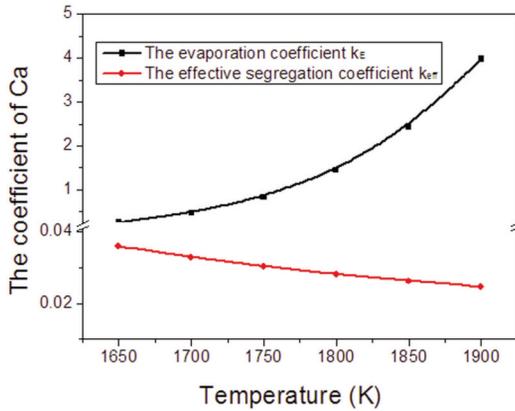


Figure 6.  $k_{eff}$  and  $k_E$  at the different temperatures

the gas-liquid interface,  $Ca(l, in Si) = Ca(g)$ , and the saturated vapor pressure of calcium can be express as follows [24]

$$\log P_{Ca}^* = -8920T^{-1} - 1.39 \log T + 14.58 \quad (1112 \sim 1756K) \quad (17)$$

According to Eq. (11) and Eq. (17),  $\gamma_{Ca}$  and  $P_{Ca}^*$  at the different temperatures were calculated, plotted in Fig. 7.

As can be seen in Fig.7, both the saturated vapor pressure of calcium and the activity coefficient of calcium increased with the temperature rising. Furthermore, the molecular thermodynamic motion is also enhanced with the temperature leading to enhancement of the diffusion of calcium in gas phase,

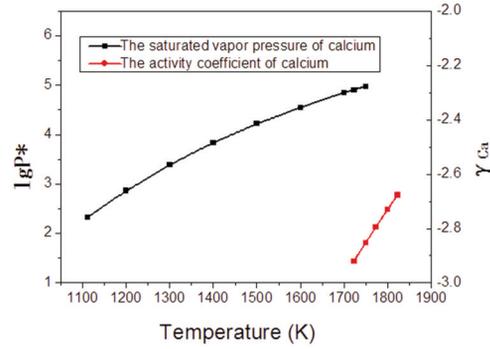


Figure 7.  $\gamma_{Ca}$  and  $P^*$  at the different temperatures

resulting in higher reaction rate. In other words, high temperature is beneficial to the evaporation of calcium. So,  $k_E$  increased in this temperature range.

Besides, it can be found that the  $k_{eff}$  slightly decreased when the temperature increase. On the one hand, the solubility of calcium in silicon increases with rising temperature, which leads to the content of calcium increases in the melt. Although the evaporation of calcium would decrease the content in the melt at the same time, which only has very little effect. The content of calcium in the melt still slightly increases so that the  $k_{eff}$  slightly decreased. On the other hand, the viscosity of melt decreased as the temperatures rising. Calcium can transfer easily to the surface of the melt, which leads to the concentration difference of calcium growing in the solid-liquid interface. Thus,  $k_{eff}$  decreased in this temperature range.

It is also notable that  $k_{eff}$  is far smaller than and  $k_E$ , and the values differ by two orders of magnitudes. Meanwhile,  $k_E$  changes significantly than  $k_{eff}$ . This suggests that the influence of temperature on  $k_E$  is much larger than on  $k_{eff}$ . Therefore, it can be concluded that calcium removal efficiency is mainly controlled by the evaporation step during vacuum directional solidification.

## 5. Conclusions

The main conclusions can be summarized as follows:

1) A mathematical model has been developed to describe calcium concentration distribution in silicon during the vacuum directional solidification as follow:

$$C_s = k_{eff} C_0 (1 - X)^{k_{eff}-1} \exp\left(-k_D k_E \frac{X}{H}\right)$$

2) UMG-Si powder with an initial purity of 99.98 wt. % was used in a vacuum directional solidification furnace. Its silicon ingot has validated successfully the mathematical model.

3) Temperature influences evaporation and segregation at the same time. As temperature rising,  $k_{eff}$  decreased but  $k_E$  increased. The comparison on the



changes of  $k_{eff}$  and  $k_E$  suggests that calcium removal efficiency is mainly controlled by the evaporation process during the vacuum directional solidification.

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