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Diffusion and mass transfer of boron in molten silicon during slag refining process of metallurgical grade silicon

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ABSTRACT

In this paper, the formulas of diffusion coefficient (D) and mass transfer coefficient (β) of boron in molten silicon were deduced. The diffusion coefficient of boron was determined to be 1.46×10^{-8} $m^2 s^{-1}$ by the diffusion experiment at 1823 K in the resistance furnace. The mass transfer process of boron between silicon and slag was described using the two-film theory and the mass transfer coefficient (β) of boron was measured to be 1.7×10^{-4} m s^{-1} while using the binary $CaO–SiO_2$ slag refining at 1823 K. It was calculated by the relation between diffusion coefficient and mass transfer coefficient that the effective boundary layer thickness (δ) close to molten silicon side was 0.086 mm.

1. Introduction

The solar-grade polysilicon used as solar cell materials is mainly produced by the chemical methods including the Siemens process and the Fluidized Bed Reactor [1–3]. As a result of some disadvantages such as high cost and heavy environmental pollution, the chemical route is being substituted by some other techniques [4,5]. The metallurgical route for a low cost solar-grade polysilicon production has gradually become a hot topic of research. In this route, the slag refining can effectively remove impurity boron from metallurgical grade silicon and most of current researches have focused on the thermodynamics of boron removal by this method [6–9]. Wu et al. [10] found that boron in metallurgical grade silicon could be removed from 18 ppmw to 1.4 ppmw using a refining technique of high basic slag. Also, the thermodynamic relation between distribution coefficient of boron (L_B) and slag activity parameter was established and confirmed. Li et al. [11] described that boron can be removed by increasing the basicity and the oxygen potential of slag. Fang et al. [12] found that the boron concentration in silicon can be decreased from 10.6 ppmw to 0.65 ppmw by $Na_2O–SiO_2$ slag refining treatment and it is beneficial for boron removal while increasing refining time under the condition of a small mass ratio of slag to silicon.

Some studies [13,14] show that the kinetic factors such as the diffusions of boron in molten silicon and borate in slag play the important roles to boron removal during the process of slag refining. The diffusion coefficient of boron in silicon melt was calculated to be 2.7×10^{-4} $cm^2 s^{-1}$ by Tang et al. [15] and it was also experimentally determined to be $(2.4 \pm 0.7) \times 10^{-4}$ $cm^2 s^{-1}$ by Kodera [16]. Based on the work of Kodera [16], Garandet [17] propose new determinations of the diffusion coefficients of various dopants in liquid silicon, and a diffusion coefficient of 1.2×10^{-8} $m^2 s^{-1}$ for boron in silicon melt was gotten. It has been reported that the rate controlling step of boron removal from metallurgical grade silicon is the mass transfer process of borate in slag. Nishimoto et al. [18] found that the boron removal rate was controlled by mass transport in the calcium silicate slag with a mass-transfer coefficient (k_S) of 1.4×10^{-6} m/s. Krystad et al. [19] had also reported the larger values for the same slag and temperature in the range of 1.7×10^{-6}–3.5×10^{-6} m/s and a relatively larger value of 4.3×10^{-6} m/s has also been obtained using the $CaO–MgO–SiO_2$ slag. Zhang et al. [20] calculated the total mass transfer coefficient of boron to be 6.85×10^{-4} cm/s for the 10% CaF_2–10%Al_2O_3–20%CaO–60%SiO_2 slag at 2073 K.

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In this paper, the diffusion coefficient of boron in molten silicon was determined by experiments. The mass transfer coefficient of boron removal using the binary CaO–SiO$_2$ slag refining was also measured and calculated. The functional relationship between boron concentration in silicon and refining time was established and confirmed. Simultaneously, the effective boundary layer thickness close to silicon side was derived from the relationship between mass transfer coefficient and diffusion coefficient of boron.

2. Theoretical formulations

The boron atoms will diffuse from solid boron toward liquid silicon when the solid boron and the liquid silicon are placed together. The concentration gradient of boron in molten silicon will be formed and distributed from the solid–liquid interface of B–Si with a high boron concentration to the molten silicon with a low boron concentration. Finally, the boron concentration in whole liquid silicon will be saturated. The schematic diagram of boron diffusion from B–Si interface to liquid silicon is shown in Fig. 1. According to Fick's second law, the diffusion rate of boron in molten silicon can be described as Eq. (1).

$$\frac{\partial c}{\partial \tau} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{1}$$

The initial and boundary conditions of differential Eq. (1) are shown in Eqs. (2) and (3).

$$c_{(x,0)} = \frac{g}{S}\delta(x) \tag{2}$$

$$\frac{\partial c_{(0,\tau)}}{\partial x} = 0 \tag{3}$$

where g and S are the total quantity and the sectional area of diffusible substance, respectively. $\delta(x)$ is the Dirac function at $x_0 = 0$. The property of Dirac function $\delta(x)$ can be expressed as Eqs. (4) and (5).

$$\delta(x - x_0) = \begin{cases} 0, x \neq x_0 \\ +\infty, x = x_0 \end{cases} \tag{4}$$

$$\int_{-\infty}^{+\infty} \delta(x - x_0)\mathrm{d}x = 1 \tag{5}$$

Then, the integral result of Eq. (1) at the initial and boundary conditions for Eqs. (2) and (3) is shown in Eq. (6).

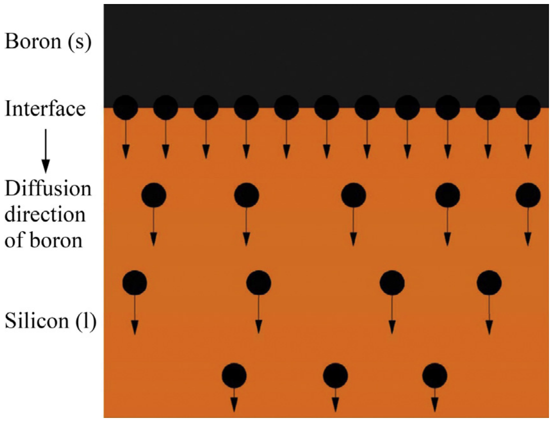

Fig. 1. Schematic diagram of boron diffusion in molten silicon.

$$c_{(x,\tau)} = \frac{g}{S\sqrt{\pi D\tau}}\exp\left(-\frac{x^2}{4D\tau}\right) \tag{6}$$

In the form of logarithm for Eqs. (6) and (7) can be gotten.

$$\lg c_{(x,\tau)} = \lg\frac{g}{S\sqrt{\pi D\tau}} - \frac{x^2}{2.3(4D\tau)} \tag{7}$$

By drawing to data, the curve of $\lg c_{(x,\tau)} - x^2$ and its slope (k) can be gotten and represented as Eq. (8).

$$k = \frac{1}{9.2D\tau} \tag{8}$$

And lastly, the diffusion coefficient of boron in molten silicon (D) can be calculated and gotten according to Eq. (8).

During the slag refining process of boron removal, there must be a silicon boundary layer (δ) and a slag boundary layer (δ'), respectively. According to the two-film theory, the oxidation and removal process of boron in silicon by the binary CaO–SiO$_2$ slag refining can be shown in Fig. 2.

According to the boundary-layer theory of convective mass transfer, the convective mass transfer rate is zero ($u_{xc} = 0$) at the verticality of phase interface, where the characteristics of mass transfer is an unsteady state diffusion. So the mass transfer rate of boron can be explained as Eq. (9):

$$J = -D\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{V}{A} \times \frac{\mathrm{d}c}{\mathrm{d}t} \tag{9}$$

Meanwhile, it can also be described as Eq. (10)

$$J = \beta(c - c^*) \tag{10}$$

Then, Eq. (11) can be obtained by Eq. (9) = Eq. (10).

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\beta \times \frac{A}{V} \times (c - c^*) \tag{11}$$

where β is the mass transfer coefficient of boron in molten silicon. A and V are the interface area of between silicon and slag and the volume of molten silicon, respectively. c and c^* are the boron concentrations in the molten silicon and at the interface of silicon-slag, respectively.

The interface concentration (c^*) can be replaced by the equilibrium concentration of boron in silicon (c_e) for a very fast reaction rate of boron oxidation at the interface of silicon-slag. After substituting the molar concentration (c) with the weight percent concentration (w[B]), Eq. (12) can be obtained by integrating Eq. (11). The value of mass transfer coefficient (β) can be described as the slope of curve.

$$\ln\frac{w[\mathrm{B}] - w[\mathrm{B}]_e}{w[\mathrm{B}]_0 - w[\mathrm{B}]_e} = -\beta \times \frac{\rho_\mathrm{m} A}{M_\mathrm{m}} \times \tau \tag{12}$$

where w[B] is the mass concentration of boron in silicon after the refining time (τ). $w[\mathrm{B}]_0$ and $w[\mathrm{B}]_e$ are the initial and the equilibrium mass concentrations of boron in molten silicon, respectively. ρ_m and M_m are the density and the mass of molten silicon, respectively.

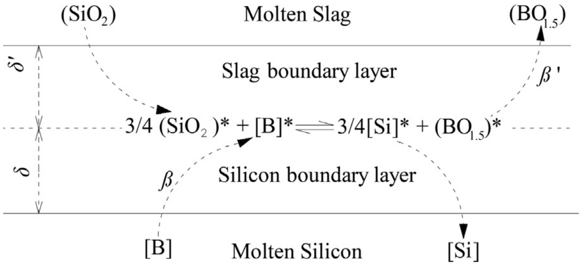

Fig. 2. Schematic diagram of boron oxidation and removal by CaO–SiO$_2$ slag.