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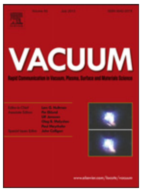

Study on the removal process of phosphorus from silicon by electron beam melting

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A B S T R A C T

According to the traditional metallurgical theory, the evaporation process of phosphorus and silicon during silicon refining by electron beam melting (EBM) is discussed and a theoretical model is established to obtain the loss rate of silicon, the removal efficiency of phosphorus and the corresponding energy consumption. The results show that phosphorus can be removed from silicon melt efficiently and quickly by EBM. There is a one-to-one correspondence between the loss of silicon and the removal efficiency of phosphorus, indicating that they have obvious effect on each other, whereas the EB power has little influence on the loss rate of silicon. If the EB power is increased from 9 kW to 21 kW, the melting time can be shortened by 68%, the loss of silicon increased by only 0.1% and the energy consumption decreased by 25%. Based on the theoretical and experimental results, a high-power EBM method is considered to be a better way for the removal of phosphorus with high efficiency and low energy consumption under such experiment conditions.

1. Introduction

The purification of metallurgical-grade silicon (MG-Si) to solar-grade silicon (SOG-Si) using metallurgical process lays the foundation for further development of the photovoltaic industry [1–3]. Compared with the chemical method, the metallurgical process is a physical process to obtain solar-grade silicon (SOG-Si). Metallurgical technology focuses on the removal of metal impurities, boron, and phosphorus, where the application of appropriate principles and technologies removes the impurities according to their properties and behaviors in silicon [4].

As an impurity element, phosphorus seriously deteriorates the electrical properties of SOG-Si and should be removed to a very low level [5]. Electron beam melting (EBM) can provide a high temperature and high vacuum environment to remove phosphorus effectively because the saturated vapor pressure of phosphorus is much greater than that of silicon [6–9]. However, silicon also evaporates under such melting conditions. The previous researches only focused on the evaporation of phosphorus without considering the evaporation loss of silicon in detail [10,11].

To provide a more convincing explanation, the present work proposed an EBM model to analyze the relationship between of phosphorus's evaporation and silicon' loss under different EB power, and the energy consumption in the same time in order to explain the purification of silicon by EBM more objectively.

2. Theoretical basis

The removal of phosphorus can be summarized by the following three steps based on the evaporation mechanism of alloying elements or impurities during electron beam melting [12]:

(1) Phosphorus transport from the molten silicon bulk to the molten/vacuum surface via the liquid boundary layer;
(2) Phosphorus evaporation from the silicon molten/vacuum interface;
(3) Phosphorus transport in gas phase away from the interface and its extraction from the vacuum system.

One or more processes of the three steps function as the rate-controlling step under different experimental conditions. The existence of severe disturbances in molten silicon under high refining temperature causes the phosphorus diffusion to be expeditious; hence, Step (1) cannot be the rate-controlling step. During electron beam melting, the mean free path of phosphorus is comparatively large and even exceeds the chamber's dimension. Thus, Step (3)

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cannot also be considered the rate-controlling step. Therefore, Step (2) is assumed to be the rate-controlling step for phosphorus evaporation. Simultaneous with the evaporation of phosphorus, silicon is lost during EBM process. The impurity contents are fairly low, and the molten silicon is the matrix of the melt. Silicon evaporation from the silicon molten/vacuum interface is thus considered as the rate-controlling step for the silicon loss.

The evaporation rate of element i under ideal electron beam melting is given by the Langmuir's equation [13]:

$$J_i = \sqrt{\frac{M_i}{2\pi RT}} \cdot P_i, \tag{1}$$

where J_i (kg m^{-2} s^{-1}) is the evaporation flux of i, M_i (kg mol^{-1}) is the mole mass of i, R (J mol^{-1} K^{-1}) is the ideal gas constant, T (K) is the absolute temperature, and P_i (Pa) is the vapor pressure of i.

The dephosphorization reaction process corresponds to the first-order kinetics and volatilizes from the molten silicon in monatomic under electron beam melting [10]. The reaction equation is

$$P(\text{mass percent in Si}) = P(\text{g}). \tag{2}$$

The Gibbs free-energy change during the process is

$$\Delta G^{\text{o}} = -RT\ln\frac{P_{\text{P}}/P_{\text{atm}}}{100\gamma_{\text{P}}W_{\text{P}}}, \tag{3}$$

where ΔG^{o} (J mol^{-1}) is the standard Gibbs free-energy change, γ_{P} is the activity coefficient of phosphorus in liquid silicon relative to one mass percent, W_{P} (%) is the mass percentage of phosphorus in molten silicon, P_{P} (Pa) is the partial pressure of phosphorus, and P_{atm} (Pa) is the standard atmospheric pressure. At low phosphorus concentration, the activity coefficient of phosphorus γ_{P} can be assumed as unity [10].

Combining Eqs. (1) and (3), the following can be obtained:

$$J_{\text{P}} = 100 \cdot P_{\text{atm}} \cdot \sqrt{\frac{M_{\text{P}}}{2\pi RT}} \cdot \exp\left(\frac{-\Delta G^{\text{o}}}{RT}\right) \cdot W_{\text{P}}, \tag{4}$$

The standard Gibbs free-energy change of phosphorous can be expressed as [10]:

$$\Delta G^{\text{o}} = 387{,}000 - 103T(\text{J/mol}). \tag{5}$$

P^{o}_{Si} is the saturated vapor pressure of silicon and substitutes for P_{Si} in Eq. (1) to calculate the silicon evaporation flux. Then

$$J_{\text{Si}} = \sqrt{\frac{M_{\text{Si}}}{2\pi RT}} \cdot P^{\text{o}}_{\text{Si}}, \tag{6}$$

The saturated vapor pressure of silicon can be expressed as [14]:

$$\log P^{\text{o}}_{\text{Si}} = -20900 \cdot T^{-1} - 0.565 \cdot \log T + 12.9. \tag{7}$$

Eq. (1) can be expressed as:

$$J_i = k_{E(i)} \cdot W_i, \tag{8}$$

where $k_{\text{E}(i)}$ (kg m^{-2} s^{-1}) is called the evaporation rate constant of i, which indicates the evaporation flux of pure liquid per unit area, per unit time. Then

$$k_{\text{P}} = 100 \cdot P_{\text{atm}} \cdot \sqrt{\frac{M_{\text{P}}}{2\pi RT}} \cdot \exp\left(\frac{-\Delta G^{\text{o}}}{RT}\right), \tag{9}$$

$$k_{\text{Si}} = \sqrt{\frac{M_{\text{Si}}}{2\pi RT}} \cdot P^{\text{o}}_{\text{Si}}. \tag{10}$$

Combining Eqs. (9) and (10) yields

$$K = k_{\text{P}}/k_{\text{Si}}. \tag{11}$$

From Eqs. (9) and (10), k_{P} and k_{Si} can be seen as a function of temperature only, and the relationship is shown in Fig. 1. With the increase in temperature, the phosphorus evaporation rate constant increases exponentially. With the same increase in temperature, the enhancement of k_{P} in a higher temperature region is more evident compared with that in a lower temperature region. Elevating the temperature favors the evaporation of phosphorus and shortens the reaction time. Similarly, the silicon's evaporation rate constant increases exponentially with increasing temperature.

The value of K indicates the intensity between phosphorus and silicon evaporation. If $K > 1$, the phosphorus evaporation is stronger than silicon evaporation, and phosphorus can be removed by electron beam melting. If $K = 1$, the concentration of phosphorus in molten silicon keeps unchanged. If $K < 1$, more silicon evaporates and phosphorus concentrates in the melt. The evaporation transfer constants of phosphorus and silicon are shown in Fig. 1 as a function of temperature. The value of K is much larger than 1, indicating that phosphorus can be removed effectively by EBM.

Based on the above analysis, the phosphorus evaporation flux increases with the increase in refining temperature, and on the condition of satisfying the requirement of SOG-Si, the refining time shortens. Therefore, production efficiency increases with the increase in refining temperature.

Meanwhile, the evaporation flux of silicon increases with increasing temperature, i.e., the acceleration of the phosphorus removal reaction is accompanied with the elevation in the silicon evaporation flux, which is contrary to the objective. However, the concern of the refining process is the total loss of silicon during the entire refining process, which is a function of time also. Under low refining temperature, the total refining time is longer than under higher temperature. The total loss of silicon depends on the refining temperature and time. So, the establishment of optimal refining process is very important to elevate the production efficiency and ensure silicon yield.

3. Electron beam melting model

The mathematical model for the removal of impurities from silicon melt during EBM process is shown in Fig. 2. The initial mass of silicon is m_0, and the silicon molten mass changed to m after refining for t time. The impurity content is as low as 10^{-3}–

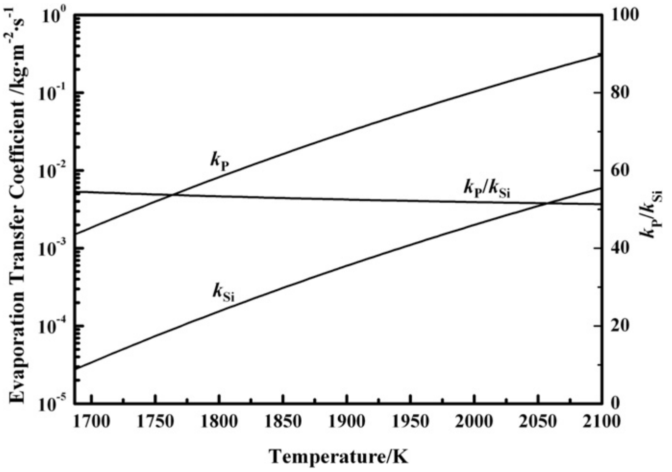

Fig. 1. Relationship between evaporation transfer constant and temperature.