

Vacuum distillation refining of metallurgical grade silicon (II) ——Kinetics on removal of phosphorus from metallurgical grade silicon

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Abstract: The kinetics on vacuum refining process of metallurgical grade silicon was studied using maximum evaporation rate, critical pressure and mean free path of phosphorus in the metallurgical grade silicon at different temperatures. The behaviors of impurity phosphorus in the vacuum distillation process were examined in detail. The results show that the fractional vacuum distillation should be taken to obtain silicon with high purity. Impurity phosphorus volatilize with the maximum evaporation rate of $1.150 \times 10^5 - 1.585 \times 10^6 \text{ g}/(\text{cm}^2 \cdot \text{min})$ in the temperature range of 1 073–2 173 K and the pressure below 2.1 Pa. Because the value of $\omega_{\text{max, P}}$ is at least 10^8 times of $\omega_{\text{max, Si}}$, Si hardly evaporates and remains in the residual, which indicates that phosphorus can be removed from metallurgical grade silicon (MG-Si) completely.

Key words: metallurgical grade silicon; solar grade silicon; vacuum distillation; kinetics; phosphorus removal

1 Introduction

Since solar cell was invented in Bell-lab, silicon was in predominant position as raw materials[1]. With the fast development of photovoltaic industry and the gradual resuscitation of semiconductor industry[2], these scraps came primarily from semiconductor industry have not meet the rapid development of solar energy industry [3]. Silicon material is one of the primary bottle-necks which impede the development of photovoltaic industry [4–5]. The metallurgical grade silicon (MG-Si) was obtained from the reduction of silica in a furnace by carbon[6]. However, MG-Si contains some impurities including Fe, Al, Ca and P and so on, which affect the physiochemical properties of silicon materials. Phosphorus is one of the impurities that are difficult to remove, and the required maximum limit for phosphorus content is 0.1×10^{-6} for solar grade silicon (SOG-Si)[7]. It is of great importance to carry out a fundamental study for solar grade silicon production. Thermodynamics on

separating impurity phosphorus from the metallurgical grade silicon by vacuum distillation was studied in our previous work[8], which solves some problems, such as the separation possibility of impurity phosphorus from metallurgical grade silicon by vacuum distillation, the separation extent and the P content of distilled metallurgical grade silicon. However, the production efficiency, namely the evaporation rate, is more important in practice. Therefore, it is necessary to study the kinetics in the vacuum distillation process of metallurgical grade silicon. It has proved that the evaporation rate of element is affected mainly by temperature and pressure. This study is aimed at the influence of temperature, pressure and free mean path on the evaporation rate of phosphorus in metallurgical grade silicon.

2 Relationship between maximum evaporation rate and temperature

When the total chamber pressure (p) is less than the

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saturation vapor pressure of a pure element (p_i^*) and the mean free path (λ) of the vaporized molecule is greater than the effective dimension (l , the distance between evaporating and condensing surface) of the unit, the evaporation rate of the distilled element is maximum, which can be described as

$$\omega_{\max} = 2.263 \times 10^{-2} \alpha p_i^* (M/T)^{1/2} \quad (1)$$

where $\omega_{\max}$ is the maximum evaporation rate, g/(cm²·min); α is the distillation coefficient; M is the relative molecular mass of the distilled element, p_i^* is the saturation vapor pressure of the distilled element, Pa; and T is the melt surface temperature, K, respectively.

The relationship between saturation vapor pressure of pure elements (p_i^* , Pa) in the metallurgical grade silicon and temperature (T , K) is listed as follows[9–10]

$$\lg p_P^* = -2740 T^{-1} + 9.965 \quad (2)$$

$$\lg p_{Si}^* = -20900 T^{-1} - 0.565 \lg T + 12.905 \quad (3)$$

Supposing that the distillation coefficient α_i is 1, the maximum evaporation rate of each element contained in the metallurgical grade silicon is calculated in the temperature range of 1 073–2 173 K according to Eqns. (2) and (3), as presented in Table 1.

Table 1 Maximum evaporation rates $\omega_{\max}$ of phosphorus and silicon at different temperatures

T/K	$\omega_{\max, Si}/(g \cdot cm^{-2} \cdot min^{-1})$	$\omega_{\max, P}/(g \cdot cm^{-2} \cdot min^{-1})$
1 073	2.196×10^{-11}	1.150×10^5
1 173	9.141×10^{-10}	1.815×10^5
1 273	2.103×10^{-8}	2.659×10^5
1 373	3.045×10^{-7}	3.673×10^5
1 473	3.051×10^{-6}	4.844×10^5
1 573	2.271×10^{-5}	6.155×10^5
1 673	1.324×10^{-4}	7.585×10^5
1 773	6.303×10^{-4}	9.114×10^5
1 873	2.533×10^{-3}	1.072×10^6
1 973	8.812×10^{-3}	1.239×10^6
2 073	2.711×10^{-2}	1.411×10^6
2 173	7.505×10^{-2}	1.585×10^6

It can be seen from Table 1 that the maximum evaporation rate is affected remarkably by the distillation temperature. The vaporation rate can be enhanced by several or even tens orders of magnitude with the temperature increment of 100 K. It is concluded that phosphorus is volatilized quickly and concentrated into vapor phase. It is easy to separate impurity phosphorus from the metallurgical grade silicon completely because the value of $\omega_{\max, P}$ is 10^8 – 10^{10} times greater than that of

$\omega_{\max, Si}$ in the temperature range of 1 573–2 173 K. Therefore, vacuum distillation can be taken to obtain silicon with lower content of P. The result is consistent with that of the thermodynamic discussion [8].

3 Influence of pressure on evaporation rate

The evaporation of metals or alloys can be promoted at vacuum atmosphere. Many studies[11–13] have shown that the evaporation rate (ω) increased with the decrease of chamber pressure (p) in a wide range ($p > p_{crit}$, as shown in Fig.1). When p reduces to a specific value or below, the ω does not increase any more or just increases at an ignorable amount. This specific value is called as critical pressure p_{crit} , which is great helpful for the selection of optimized pressure. The critical pressure means that ω is the $\omega_{\max}$ in practice. It rises with enhancing temperature.

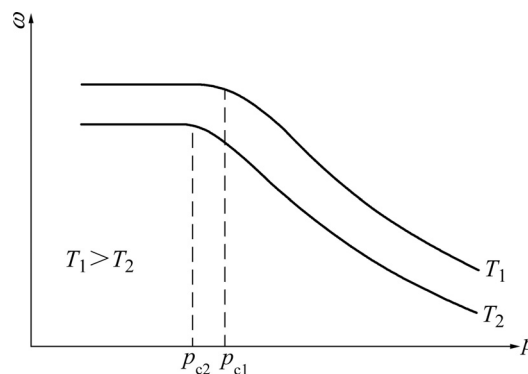


Fig.1 Relationship between evaporation rate and chamber pressure

The critical pressure is determined by a useful scattering cross-section of vapor molecular and its mass as[10]

$$p_{crit} = \frac{\kappa T}{\lambda \sigma \sqrt{1 + \frac{M_m}{M_g}}} \quad (4)$$

$$\sigma = \frac{\pi}{4} \left(\frac{d_m + d_g}{2} \right)^2 \quad (5)$$

where M_m is the relative molecular mass of the metal vapor, M_g is the relative molecular mass of the residual gas vapor, d_m is the diameter of the metal vapor molecular, d_g is the diameter of the residual gas vapor molecular, σ is the mean useful cross-section of the vapor molecular, κ is Boltzmann constant ($\kappa = 1.38 \times 10^{-23}$ J/K), and λ is the mean free path, respectively.

During the experiment, we used argon as the protective gas and the distance between evaporating and

condensing surface is 15 cm in vacuum distillation for MG-Si refining. It is considered that argon is the residual gas and λ is 15 cm. Thus, the critical pressures of the phosphorus in the MG-Si calculated by Eqns.(4) and (5) on basis of the values of M_m , M_g , d_m and d_g are listed in Table 2.

Table 2 Relationship between critical pressure p_{crit} of pure metal and temperature

T/K	$p_{\text{crit, Si}}/\text{Pa}$	$p_{\text{crit, P}}/\text{Pa}$	T/K	$p_{\text{crit, Si}}/\text{Pa}$	$p_{\text{crit, P}}/\text{Pa}$
1 073	1.761	2.121	1 673	2.745	3.307
1 173	1.925	2.319	1 773	2.909	3.505
1 273	2.089	2.516	1 873	3.073	3.702
1 373	2.253	2.714	1 973	3.237	3.900
1 473	2.417	2.912	2 073	3.401	4.098
1 573	2.581	3.109	2 173	3.566	4.295

It is shown from Table 2 that the critical pressure is related to the evaporation temperature, and p_{crit} enhances with the increase in temperature. The value of $p_{\text{crit, Si}}$ is 1.761–3.566 Pa in the temperature range of 1 073–2 173 K, and the value of $p_{\text{crit, P}}$ is 2.121–4.295 Pa in the temperature range of 1 073–2 173 K. The minimum chamber pressure should be less than 2.1 Pa to ensure the maximum evaporation rate of P reach the range of 1.150×10^5 – 1.585×10^6 g/(cm²·min) while the silicon volatilizes at lower rate far less than the $\omega_{\text{max, P}}$. Because the value of $\omega_{\text{max, P}}$ is at least 10^8 times of $\omega_{\text{max, Si}}$, Si hardly evaporates and remains in the residual. Phosphorus could be separated from MG-Si completely.

4 Effect of temperature and pressure on mean free path

As mentioned above, the mean free path (λ) of the distilled vapor molecule is greater than or equals to the effective dimension (l) of the chamber, under which the evaporation rate is not affected by chamber pressure any more. When the vapor molecular of distilled silicon is considered as monatomic one, the effect of temperature and pressure on mean free path can be described as[14]

$$\lambda = \frac{3.11 \times 10^{-18} T}{d^2 p} \quad (6)$$

where p is the chamber pressure, Pa; and d is the diameter of phosphorus vapor molecular, $d_p = 2.46 \times 10^{-8}$ cm.

According to Eqn.(6), the mean free path values of distilled phosphorus vapor molecular are calculated in the temperature range of 1 073–2 173 K and pressure 0.001–10 Pa, as shown in Fig.2.

It can be seen from Fig.2 that the minimum

distillation pressure can be controlled in 0.5–1.0 Pa for matching l at the temperature of 1 773 K. The minimum pressure is considered the critical pressure of the condition above. Phosphorus evaporates quickly at the maximum rate of 1.150×10^5 – 1.585×10^6 g/(cm²·min). The evaporation rate does not increase with lowering distillation pressure. Also from Fig.2, λ increases with enhancing temperature, which indicates that p_{crit} behaves in the same way.

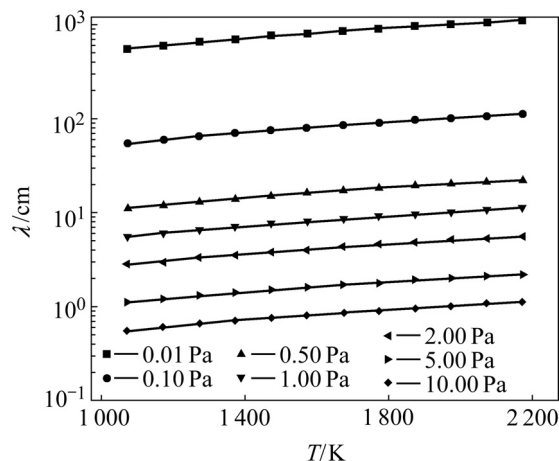


Fig.2 Mean free path of distilled phosphorus vapor molecular

Therefore, the evaporation rate of metal relates to distillation temperature as well as the value of residual pressure. It is necessary to control the elevated temperature and low chamber pressure for separating impurity phosphorus efficiently from the silicon in the process of MG-Si refining.

5 Conclusions

- 1) It is an effective route to remove phosphorus using vacuum distillation for MG-Si refining.
- 2) Impurity phosphorus volatilizes at the maximum evaporation rate of 1.150×10^5 – 1.585×10^6 g/(cm²·min) in the temperature range of 1 073–2 173 K and the pressure below 2.1 Pa.
- 3) Because the value of $\omega_{\text{max, P}}$ is at least 10^8 times of $\omega_{\text{max, Si}}$, Si hardly evaporates and remains in the residual. Phosphorus can be separated from MG-Si completely.

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