Study on Phosphorus Removal from Metallurgical Grade Silicon by Vacuum Distillation

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Abstract: There was a dramatic increament about 30% per year in photovoltaic industry in recent years. And the raw material of photovoltaic industry is impossible to increase markedly within next 10 ~ 15 years. Therefore, it is inevitable to establish an independent feedstock system of solar grade silicon (SOG-Si) material. In this paper, a theoretical analysis about the feasibility of phosphorus removal in metallurgical grade silicon with vacuum distillation, then an experiment was conducted.

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

Since solar cell was invented in Bell-lab, silicon has been in predominant position as its raw material. The raw material of solar cell came primarily from scraps of semiconductor industry. These scrapes were re-melted and casted to manufacture solar cell wafer. During the recession of semiconductor industry, it was very important for this kind of raw material supply system. However, with the fast development of photovoltaic industry and the gradual resuscitation of semiconductor industry, these scraps have not been satisfied the normal development of solar energy industry. For the further development of solar cell industry, it is necessary to produce low cost SOG-Si with a raw material supply system which was independent from the semiconductor industry. In metallurgical grade silicon (MG-Si), phosphorus was one of the impurities that were difficult to remove. According to the characteristics of phosphorus, vacuum distillation was conceived to remove phosphorus in MG-Si. Some elementary experiments have been conducted to investigate this method and provide useful information for further research[1-6].

2 Theoretical analysis

Relationship between the saturated pressure and temperature is shown in equation 1.

$$\lg P = AT^{-1} + B\lg T + CT + D \quad (1)$$

Where, A, B, C and D denote coefficients respectively, as shown in Table 1.

According to equation 1, saturated pressure of liquid of different substance can be worked out at a given temperature. Fig. 1 presented the relationship between lgP and T for phosphorus and silicon, which is a high saturated pressure for phosphorus with low volatile rate at atmosphere pressure, and is low saturated pressure for silicon, which meant it is difficult for silicon to volatile into gas from raw material at atmosphere pressure. At 1732 K, silicon began to melt and phosphorus sublime. Saturated pressure of phosphorus exceeds 10^8 Pa, which means it would be distilled out of the silicon. As a result, theoretically, phosphorus and silicon could be separated using vacuum distillation.

Tab. 1 The values of coefficients of A, B, C and D[7]

Element	lg P/Pa A	B	C × 10³	D	T/K
$P_{(red)}$ $P_{(white)}$	−2740	—	—	9.965	M.P. ~ B.P.
Si	−20900	−0.565	—	12.905	M.P. ~ B.P.

Note: M.P., melting point; B.P., boiling point

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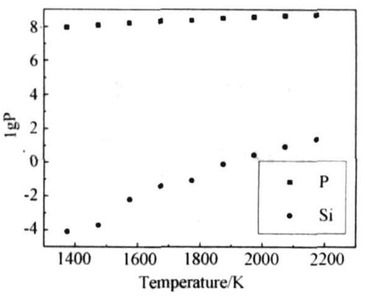

Fig. 1 Relationship between saturated pressure and temperature for pure substance

3 Phase balance

For A-B binary alloy, $X_{A,g}$ and $X_{B,g}$ indicated the mass ratio of substance A and B in gas phase, and $X_{A,l}$ and $X_{B,l}$ indicated the mass ration of substance A and B in liquid phase respectively. Obviously, $X_{A,g}+X_{B,g}=1$ and $X_{A,l}+X_{B,l}=1$, then following equation 2 and equation 3 can be calculated.

$$X_{A,g}=\left[1+(X_{B,l}/X_{A,l})\cdot(\gamma_B/\gamma_A)\cdot(P_B^*/P_A^*)\right]^{-1} \quad (2)$$

$$X_{B,g}=\left[1+(X_{A,l}/X_{B,l})\cdot(\gamma_A/\gamma_B)\cdot(P_A^*/P_B^*)\right]^{-1} \quad (3)$$

According to the content of impurities in silicon, the principles and degree about the separation of impurities can be found out through phase diagram. In Si-i system, γ_{Si} was approximately equal to 1. Then according to equation 2 and equation 3, liquid-gas phase graph of two binary alloy system can be shown as in Fig. 2. As the presented in Fig. 2, at temperature of 1673 K, 1773 K and 1873 K, phosphorus content in gas phase were all approximately equal to 100%, which indicates that separation of phosphorus and silicon could be realized when phosphorus volatile into gas phase completely through vacuum distillation.

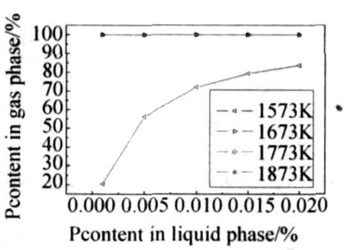

Fig. 2 Equilibrium diagram of Si-P binary system

4 Experiments

The raw material was screened solid powder of MG-Si. Vacuum distillation was conducted in the vacuum furnace, whose schematic diagram was presented in Fig. 3.

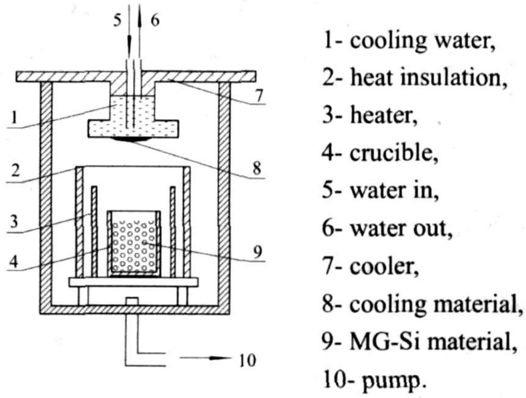

Fig. 3 Schematic diagram of experimental setup

As shown in Fig. 4, volatile rate increased with the increase of distillation time, which indicates the decrease of phosphorus content in residual slag. The maximum removal efficiency could be above 97.3%, which shows that there is a good agreement between the experimental results and the theoretic analysis.

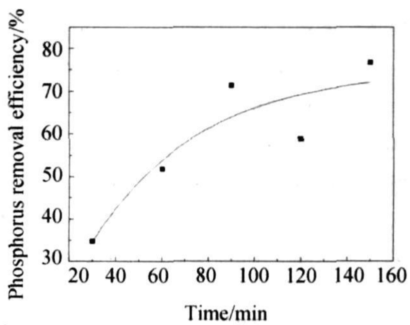

Fig. 4 Influences of distillation time on removal efficiency

5 Conclusions

At 1723 K, the longer the distillation time is, the higher the phosphorus removal efficiency will be, and the maximum removal efficiency could be above 97.3%.

Small phosphorus content in residual may partly due to the same compound phosphorus existed in silicon. Existence of phosphorus steam in gas phase may also contribute the low phosphorus content in the residual.

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冶金级硅真空蒸馏除磷研究

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摘　要：近几年，光伏产业以 30% 的速度持续强劲增长。作为原料的半导体工业副产品供应的不足并且在未来 10～15年内也不能显著增加的情况下，建立独立的太阳能级高纯硅原料供应体系是不可避免的。从理论上分析了利用真空蒸馏的方法除磷提纯冶金级硅的可行性，并进行了真空条件下脱磷的实验研究。

关键词：太阳能级硅；冶金级硅；真空蒸馏；除磷
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