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# Boron removal from metallurgical grade silicon by oxidizing refining

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**Abstract:** A purification process was developed to remove impurity element boron from the metallurgical grade silicon by the electric arc furnace refining. The thermodynamic equilibria calculation and experiment to remove boron in the oxidizing atmosphere were performed and analyzed. Boron is removed as the gaseous species $B_xO_y$ and $B_xH_zO_y$ in $O_2$ and $H_2O$-$O_2$ atmosphere respectively. The equilibrium pressure of $B_xH_zO_y$ is $10^5$−$10^{10}$ times that of $B_xO_y$. Boron is removed and its content in silicon is reduced from $18\times 10^{-6}$ to $2\times 10^{-6}$ in the Ar-$H_2O$-$O_2$ atmosphere in the electric arc furnace.

**Key words:** thermodynamics; metallurgical grade silicon; purification; oxidizing refining; electric arc furnace

## 1 Introduction

Since 2000, the booming of photovoltaic (PV) industry has being lasted for about 8 years. The worldwide production of photovoltaic modules was 1 787 MW in 2005 and it is projected to approach 18 GW annually by 2020. In 2005, more than 90% of the solar cells were made using crystalline silicon. The growth of the PV industry is limited by the availability of silicon feedstock, and is directly dependent on the electronic industry processes. In other words, the photovoltaic industry will face a shortage of silicon feedstock in the near future[1−3]. At present, the supply of solar grade silicon is short of demand and the new technique of production and purification with large scale and low price must be explored. The purification of metallurgical grade silicon is being paid close attention by investigators.

Impurity elements Fe, Al, Ca, Ti, P, B, etc, in silicon can be removed by the metallurgical method. Among them, the metallic elements with very small segregation coefficient can be separated from silicon by the directional solidification[4]. B and P contents in silicon materials will affect the conversion efficiency of solar grade cells. Phosphorus can be volatilized from silicon in form of high volatile $P_2$[5]. But the boron removal is still a challenge for its large segregation coefficient to silicon ($k_0$=0.8) and low vapor pressure ($p_B$=$10^{-6}$ Pa at 1 773 K)[6−7]. The common practice of boron removal is by pyrometallurgical refining step with the calcium silicate slag of CaO-$SiO_2$, CaO-$Al_2O_3$-$SiO_2$ or $NaO_{0.5}$-CaO-$SiO_2$ to obtain solar grade silicon[8−11]. Plasma refining is restricted for the apparatus despite of its availability in boron removal[12−13]. Even though, boron can be also vaporized from silicon in form of gaseous oxides or hydrates[14].

In this work, the oxidizing refining method of metallurgical grade silicon was used for the boron removal and the process and feasibility were presented. Based upon the thermodynamic equilibria analysis of molten silicon system in $O_2$ and $H_2O$-$O_2$ atmosphere, it is demonstrated that the boron content in metallurgical grade silicon can be effectively reduced. And the experimental setup and results were presented.

## 2 Thermodynamic equilibrium analysis

The thermodynamic equilibrium analysis aims at the form and limit of boron removal by calculating the Gibbs free energy and vapor pressure of gaseous species at different temperature, and determining system pressure

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and gas composition, therefore, to provide a guideline or reference for oxidizing refining application of metallurgical grade silicon. The melting and boiling points of Si and B are 1 685, 2 540 and 2 573, 2 820 K, respectively. Silicon is in molten state at the determinate temperature range of 1 685−2 500 K. Boron oxides BO, $B_2O$, $BO_2$, $B_2O_2$, $B_2O_3$ and hydrates BHO, $BH_2$, $BHO_2$, $BH_2O_2$, $BH_3O_3$, $B_2H_4O_4$, $B_3H_3O_3$, $B_3H_3O_6$ are volatile according to the thermodynamic data. So, the impurity element boron in metallurgical grade silicon can be changed into gaseous species through oxidization in $O_2$ and $H_2O$-$O_2$ atmosphere and then be removed. The effects of other impurities elements such as Fe, Al, Ca, Ti, P, C, Cu, V, etc, on Si and B are ignored here.

### 2.1 Oxidizing refining of $O_2$ atmosphere

The impurity element boron dissolved in molten silicon and expressed as [B] is oxidized into gaseous boron oxide species ($B_xO_y$) by $O_2$ in the temperature range of 1 685−6 000 K. The potential reactions in [B]-$O_2$ and Si-$O_2$ are listed in Table 1.

**Table 1** Reactions for Si-B-O system

| Number | Reaction | Temperature range/K |
|---|---|---|
| (1) | $2[B]+O_2 = 2BO(g)$ | 1 685−6 000 |
| (2) | $[B]+O_2 = BO_2(g)$ | 1 685−6 000 |
| (3) | $4/3[B]+O_2 = 2/3B_2O_3(g)$ | 1 685−6 000 |
| (4) | $4[B]+O_2 = 2B_2O(g)$ | 1 685−6 000 |
| (5) | $2[B]+O_2 = B_2O_2(g)$ | 1 685−6 000 |
| (6) | $Si(l)+O_2 = SiO_2(l)$ | 1 685−3 504 |
| (7) | $2Si(l)+O_2 = 2SiO(g)$ | 1 685−3 504 |

Based on the handbook of NIST-JANAF Thermochemical Tables[15], the relationship between the Gibbs free energy change ($\Delta G^\Theta$) of chemical oxides ($B_xO_y$, $SiO_2$, SiO) and temperature ($T$/K) was calculated and shown in Fig.1, where the preferential order of oxidizing products is $B_2O_3 > B_2O_2 > BO > BO_2 > B_2O$. The $\Delta G^\Theta$ values of $SiO_2$ and SiO are much negative in the temperature range of 1 685−2 100 K and 2 100−2 500 K, respectively. The silicon is the principal part in the molten system and the reactions (6) and (7) firstly occur at 1 685−2 100 K and 2 100−2 500 K, respectively. According to Fig.1, we conclude that the impurity element B in metallurgical grade silicon may not be oxidized into gaseous species at 1 600−2 500 K and at this temperature region only Si oxidation takes place to form $SiO_2$ and SiO.

The $\Delta G^\Theta$—$T$ curve of gaseous boron oxides ($B_xO_y$) is declined downwards and opposite to that of $SiO_2$. The reactions (8)−(12), given in Table 2, between $SiO_2$ and [B] will occur at the determinate temperature and pressure.

The relationship between $\Delta G^\Theta$ and $T$ of the reactions (8)−(12) is shown in Fig.2.

**Table 2** Reactions between $SiO_2$ and [B]

| Number | Reactions | Temperature range/K |
|---|---|---|
| (8) | $(SiO_2)+2[B]=Si(l)+2BO(g)$ | 1 685−3 504 |
| (9) | $(SiO_2)+[B]=Si(l)+BO_2(g)$ | 1 685−3 504 |
| (10) | $(SiO_2)+4/3[B]=Si(l)+2/3B_2O_3(g)$ | 1 685−3 504 |
| (11) | $(SiO_2)+4[B]=Si(l)+2B_2O(g)$ | 1 685−3 504 |
| (12) | $(SiO_2)+2[B]=Si(l)+B_2O_2(g)$ | 1 685−3 504 |

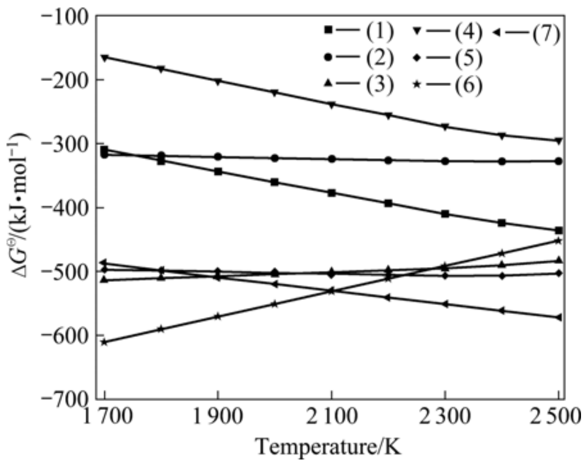


**Fig.1** $\Delta G^\Theta$ of oxides vs temperature for Si-B-O system (reacting gas: $O_2$)

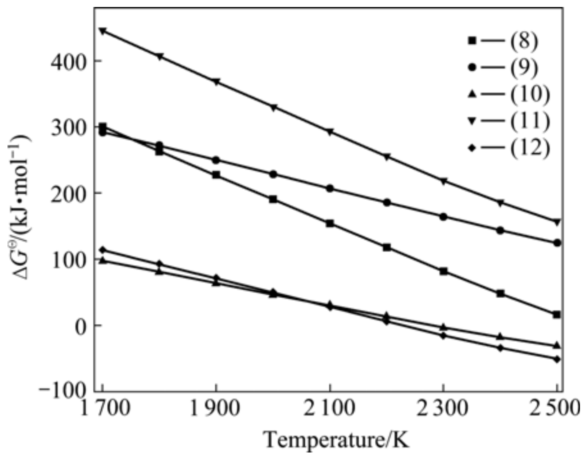


**Fig.2** $\Delta G^\Theta$ of reactions between $SiO_2$ and [B] vs temperature

From Fig.2, the $\Delta G^\Theta$ values of reactions (8)−(12) are all positive below 2 300 K. It is possible to reach the negative $\Delta G^\Theta$ values by changing system pressure. The impurity boron is then oxidized into gaseous oxides ($B_xO_y$) by the production of $SiO_2$ and the reactions (8−12) are generally expressed as

$$(SiO_2)+\frac{2x}{y}[B]=Si(l)+\frac{2}{y}(B_xO_y)(g) \quad (13)$$