The removal of phosphorus and boron by slag and acid leaching treatment

Falin HE[1]
College of Physics and Mechanics and Electrics
Xiamen University, 361005 Xiamen, P R China
e-mail:linfahe@163.com

Chao CHEN[2*]
School of Energy Research
Xiamen University, 361005 Xiamen, P R China
e-mail: cchen@xmu.edu.cn
*Corresponding author

Abstract*—The rapid development of photovoltaic industry is causing many researches on the refining of silicon, especially the purification of silicon by metallurgical method from the metallurgical-grade silicon (MG-Si). The removal of phosphorus and boron is one of the major problems on the refining of MG-Si to Solar-grade silicon (SoG-Si). At present, the removal method of phosphorous and boron by slagging of CaO-SiO$_2$-CaF$_2$ and acid leaching treatment is being researched. It was found that the best removal ratio of phosphorous and boron could reach up to 81% and 92%. Meanwhile, the principle of removal of phosphorous and boron has been studied. *(Abstract)

Keywords-metallurgical-grade silicon; phosphorus; boron; slagging; acid leaching

I. INTRODUCTION

More and more attention has been paid to the solar energy for its wider distribution and infinite storage, the solar power is cleaner than the traditional energy, and has become one of the major directions of the development of energy for humankind. From 2000 to 2009, the global photovoltaic (PV) power installed capacity showed an increasing tendency with an annual increase of 45%, by the end of 2009, the global cumulative installed PV system has reached 21.3 GM [1]. Solar grade poly-silicon has become the main feedstock for solar cells because of its low cost, low pollution, and low energy consumption. In the year of 2008 the production of global solar grade poly-silicon has reached 43500 tons, accounting for 65% of the global poly-silicon (EG and SoG) [2]. Since 2002, S.Dewolf and J.Szlufcilk et al [3] have made the solar cells with the efficiency of 12.38% out of the solar grade poly-silicon which was purified by metallurgical method; it is a hot-spot to make solar cells with the low cost poly-silicon produced from the metallurgical method [4-5].

Phosphorus is one of the main impurities of silicon. The present domestic and foreign research progresses on phosphorus removal from silicon by metallurgical method mainly includes alloy unidirectional solidification, vacuum refining processes and electron beam melting [6-8]. Because of the high melting point, small segregation coefficient and small saturated steam pressure coefficient, it's difficult to remove boron from silicon. The method of removing boron mainly includes slagging [9], plasma treatment [10], and alloy solidification [11]. In present work, the MG-Si is handled by slag and acid extraction respectively. The formation mechanism of compound of phosphorous and boron in silicon boundary has been investigated, as well as the relationship between cooling rate of molten silicon and removal rate of phosphorous has been discussed.

II. EXPERIMENT

A. Sample preparation

The melting experiments have been carried out in an induction furnace. A graphite crucible with inner diameter of 55 mm and depth of 90mm is positioned inside the induction coil in the center part of the furnace. MG-Si and reagent grade CaO、SiO$_2$ and CaF$_2$ powder have been used as raw materials. Different amount of CaO (mass 50%) -SiO$_2$ (mass 40%) - CaF$_2$ (mass 10%) slag have been mixed with 100 g MG-Si completely. Then the mixture is added in the graphite crucible. Each experiment is carried out in the protective Ar gas atmosphere of 20000 Pa and temperature of 2073 K for 1800 s. The molten silicon and CaO-SiO$_2$- CaF$_2$ cooling is processed at different speeds in the graphite crucible. Then the obtained ingot is cut into two pieces, one piece is crushed and grounded into powder of 100-120 mesh for Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analyses, the other one is polished on the profile for Electron Probe Micro-Analyzer (EPMA) analyses.

B. Acid leaching treatment

Acid leaching treatment has been employed on both the powder and the profile. The powder with particles of 100-120 microns is added in a Poly-tetra-fluoro-ethylene (PTFE) container, acid with a certain concentration is poured in the PTFE container to immerse the powder in acid. Then the PTFE container is put in the water with temperature of 353 K for some time, after that, the powder is washed by deionized water. This is one cycle of acid leaching. Acids of HCl, Aqua Prepare Your Paper Before Styling regia and HF acid have been used for the leaching cycle for 24h, 12h and 12h, respectively. After three cycles of acid leaching, the powder is cleaned with deionized water and dried for ICP-OES analyses. As well as the profile of the half piece is leached with one cycle of HCl acid for 4h, and cleaned by deionized water for EPMA analyses.

III. RESULTS AND DISCUSSION

A. Silicon slagging with CaO-SiO_2-CaF_2

The MG-Si is slagged with different amount of CaO-SiO_2-CaF_2, and analyzed by ICP-OES. The concentrations of phosphorous and boron in MG-Si are listed in Table 1.

TABLE I. THE CONTENT OF P AND B IN MG-SI AFTER SLAGGING WITH DIFFERENT AMOUNT OF CaO-SiO_2-CaF_2.

sample / elements	*MG-Si*	*MG-Si +a% slag*	*MG-Si +b% slag*	*MG-Si +c% slag*
P	25.32	18.02	20.99	18.53
B	6.49	1.11	2.92	3.33

Note: the slag is CaO(mass 50%) -SiO_2 (mass 40%)- CaF_2 (mass 10%) and the values of a、b and c is a>b>c. All values are in ppmw.

From the Table I, we can see that the concentration of phosphorous and boron in MG-Si have been reduced after slagged with different amount of CaO-SiO_2-CaF_2. The removal ratio of boron increases when the content of slag agent increases. Because the boron could be oxidized into boric acid ion by the slag of CaO-SiO_2-CaF_2 and the boric acid ion is diffused into the slag, so the boron could be separated from the MG-Si. The more content of slag the more boron can be oxidized. The phosphorous precipitation phase in grain boundary is shown in Fig. 1, which is scanned by EPMA mapping.

From the Table II, the segregation coefficient of phosphorous and boron is close to one [12-13], and that of calcium is far less than one. Generally speaking, during the cooling of MG-Si, the phosphorous and boron are almost not precipitated in the grain boundary, because of they segregation coefficient. Accounting to the action of slag, some of the phosphorous (or boron) dissolved in slag, the other precipitated in the grain boundary with Ca. As is shown in Fig. 1, after slag there are some content of phosphorous and boron precipitated in grain boundary.

TABLE II. SEGREGATION COEFFICIENT OF IMPURITIES IN SILICON [12-13]

impurities	*segregation coefficient*
B	8.00×10^{-1}
Al	2.80×10^{-3}
P	3.50×10^{-1}
Ca	$(1.3\text{-}5.2)\times10^{-4}$
C	5.00×10^{-2}
Ti	2.00×10^{-6}
Fe	6.40×10^{-6}
Cu	8.00×10^{-4}

Tomohi Toshimpo and Gen Inoue et al. investigated the interaction coefficient of phosphorous (or boron) and calcium, and reported that the values of interaction coefficient of phosphorous and boron with calcium in molten silicon (1732K) are shown as follows [14-15].

$$\varepsilon_{Ca}^{P} = -14.6 \pm 1.7$$

$$\varepsilon_{Ca}^{B} = -3.08 \pm 0.84$$

Min and Sano reported that calcium and phosphorous formed a stable compound (i.e., Ca_3P_2) [16]. Owing to the fact that the value of interaction coefficient of boron and calcium in molten silicon is negative, the boron also may be pulled into the grain boundary and formed a certain stable compound. In the grain boundary of MG-Si the phosphorous (or boron) and Ca formed the alloy phase, which precipitated in the Si-Ca alloy. The values of the interaction coefficient phosphorous and boron are negative. In other words, the attraction force between phosphorous (or boron) with calcium is larger than that with silicon. When the molten silicon cool the phosphorous (or boron) is pulled to grain boundary by calcium.

B. Acid leaching treatment

MG-Si slagging with different amount of CaO-SiO_2-CaF_2, then do the process of acid extraction, which mentioned in experiment and the concentration of phosphorous and boron are analyzed by ICP-OES (listed in Table III).

TABLE III. THE CONCENTRATION OF P AND B AFTER ACID LEACHING TREATMENT. ALL VALUES ARE IN PPMW.

sample / elements	*MG-Si*	*MG-Si +a% slag*	*MG-Si +b% slag*	*MG-Si +c% slag*
P	21.43	4.02	8.45	4.04
B	6.21	0.65	0.70	3.08

Note: the slag is CaO(mass 50%) -SiO_2 (mass 40%)- CaF_2 (mass 10%) and the values of a、b and c is a>b>c.

After slagging with CaO-SiO_2-CaF_2, the content of Ca in MG-Si samples increase obviously and Ca becomes the main impurity, and then the precipitation phases have been change from Si-Fe-base alloy to Si-Ca-base alloy. As is shown in Fig.2, the Si-Ca and Si-Ca-base precipitation phases can be removed by HCl acid leaching completely. At the same time the phosphorous (or boron) and calcium compound, which precipitated in Si-Ca or Si-Ca-base alloy, also can be removed by inorganic acid rapidity. So phosphorous and boron could be removed by acid leaching treatment.

C. Effect of removing ratio and cooling rate

MG-Si slagging with CaO (mass 50%) -SiO_2 (mass 40%) - CaF_2 (mass 10%), which the value of slag/silicon is one, and the molten silicon and slag cool at different speeds, then they are crushed to 100-120 microns and processed by acid leaching treatment. Finally, the powder is analyzed by ICP-OES. The concentrations of phosphorous and boron are listed in Table IV.

TABLE IV. THE CONTENT OF P AND B AFTER SLAGGING WITH DIFFERENT COOLING RATE. ALL VALUES ARE IN PPMW.

cooling rate / element	slow	medium	fast
P	3.20	6.85	8.74
B	1.02	1.14	1.08

Note: the slag is CaO(mass 50%) -SiO_2 (mass 40%)- CaF_2 (mass 10%) and the values of a、b and c is a>b>c.

From the Table Ⅳ, it indicates that the cooling rate has little influent on the removal rate of boron, but it has dramatic implications in removing phosphorous. This may be due to the fact that too quick cooling will hinder the process of phosphorous precipitation to the grain boundaries under the effect of calcium.

IV. CONCLUSIONS

In the present paper, the removal of phosphorous and boron by slag and acid leaching treatment have been researched. To conclude:

1).The removal rate of boron is decided by the content of slag agent. The more content of slag agent is added into the molten silicon, the higher the boron removal rate is.

2).The effect of removal of phosphorous has close relationship with cooling speed of molten silicon, which has slag. The more slowly the cooling speed of molten silicon and slag is the better effect the removal of phosphorous after acid leaching treatment.

3).The removal rate of boron has nothing to do with cooling speed of molten silicon.

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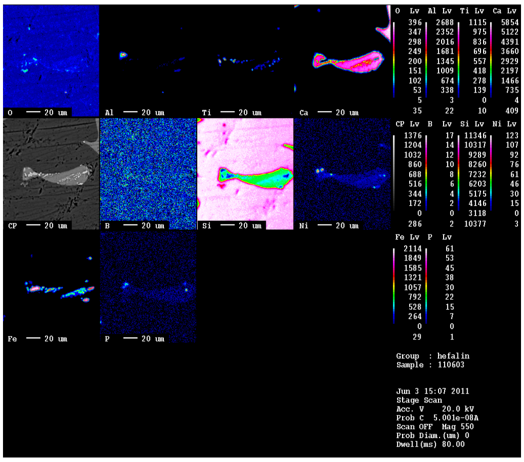
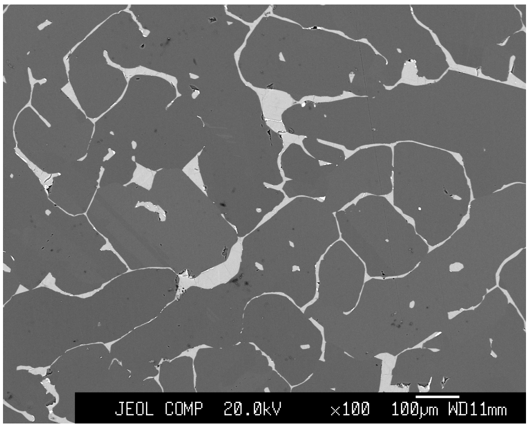
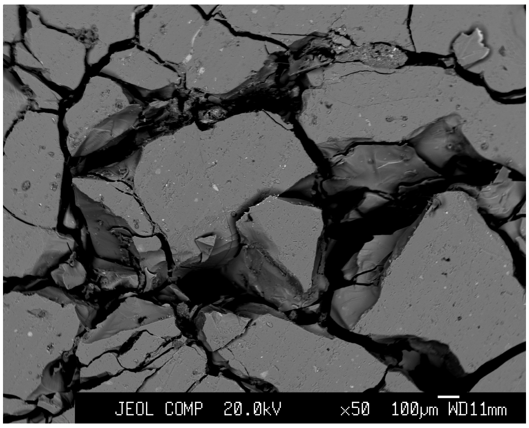


Figure 1. EPMA mapping sample after slag



(A) Before leaching



(B) After leaching in HCl 4mol/L 80℃ 4 hours

Figure 2. Microstructure of MG-Si after slagging