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Enhanced separation of phosphorus from metallurgical grade silicon by $CaAl_2Si_2$ phase reconstruction

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ABSTRACT

To find a high-efficiency approach for removing phosphorus from metallurgical grade silicon, a novel method of silicon-aluminum-calcium alloy refining was investigated through phase reconstruction to form $CaAl_2Si_2$ phase. The distribution of phosphorus between purified solid silicon and liquid silicon-aluminum-calcium alloy was determined to investigate the possibility of removing phosphorus from the silicon by alloy refining with silicon-aluminum-calcium melt. It was found that the $CaAl_2Si_2$ phase had a high affinity for phosphorus resulting in dissolving a large quantity of phosphorus. Decreasing the amount of getter materials was not good for the phosphorus removal from the silicon, while adopting twice alloy refining could strengthen the removal with obtaining as high as 99.99 wt% purity silicon. In addition, the purity of refined silicon depends on the quenching temperature and the cooling rate. Moreover, to evaluate efficiency of phosphorus removal from silicon by silicon-aluminum-calcium alloy refining, the thermodynamic properties of phosphorus in solid silicon and liquid alloy phase at 1273–1473 K were further evaluated by the chemical equilibrium method.

1. Introduction

The slather using of the energy, especially the traditional fossil energy resources, brings and accelerates the appearance of many environmental problems, such as the stratosphere fog haze, the destruction ozone layer and the global warming. As a consequence, much attention is being paid to the renewable and clean energy – solar energy. However, the high price of solar cells has become a critical limiting factor for the widespread use of solar energy even with governmental subsidies. For this reason, in order to make solar cells less expensive, it is considered to be one of the feasible ways to utilize relatively inexpensive metallurgical grade silicon (MG-Si, 99 wt% pure) as a starting material for directly making solar grade silicon (SOG-Si, 99.999 wt% pure).

Since deteriorating the electrical properties of silicon materials, such as electrical resistivity and minority carrier lifetime, Phosphorus (P), one of the typical harmful impurities in MG-Si, should be reduced to lower than 0.1 ppmw for solar cells applications. As featuring relatively large segregation coefficient between solid and liquid silicon (0.35) [1], P is difficult to remove by directional solidification, which is believed to be the final step of metallurgical purification routes. On the other hand, vacuum refining is a comparatively effective way to remove P from MG-Si melts due to its high vapor pressure in molten silicon [2–4]. Zheng et al. [5] reported that in a pilot-scale experiment, smelting for 2 h, P concentration in MG-Si was decreased from 15 ppmw to 0.08 ppmw at the condition of the temperature ranged from 1773 K to 1873 K and the vacuum from 0.1 to 0.035 Pa, which achieved the target for SOG-Si of less than 0.1 ppmw. However, the issues of high-cost equipments and large energy consumption make this method non-attractive; furthermore, the high lose of silicon should also be resolved. Slag treatment is another efficient method proposed for removing boron (B) and P from the impure silicon [6–9]. Meteleva-Fischer et al. [8] reported that the P concentration in MG-Si was successfully reduced to the concentrations below the detection limit of ICP-OES (less than 1 ppmw) after slag treatment for 1 h at 1743 K when the mass ratio of the $CaO\text{-}SiO_2$-20.8 wt% Na_2O slag to MG-Si was 2.3 and acid leaching (HF + HCl: 20 wt%; particle size: 100 μm). Meanwhile, Jung et al. [9] conducted slag treatment to remove P from MG-Si by using $CaO\text{-}SiO_2\text{-}CaF_2$ slag with the ratio of slag to silicon of 2, and more than 90% of P was eliminated after 12 h of slag treatment at 1773 K. However, the refined silicon will always be contaminated with the impurity elements introduced by slag phase, forming silicon-based precipitated phases deposited at the grain boundary. Thus, acid leaching is generally applied to separate the refined silicon from the

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precipitations. Nevertheless, the slag treatment for achieving high removal efficiency of P requires high-temperature operation for a long time; moreover, a high ratio of slag to silicon will be required. A more economical and high-efficiency method is preferred.

Recently, alloy refining, as a promising method for upgrading MG-Si at relatively low refining temperatures, has attracted considerable attention. This method uses a metallic agent as a solvent for trapping impurities in impure silicon. The refined silicon will recrystallize as the primary silicon phase through silicon-metal melt when the melting temperature cools below the liquidus; meanwhile, impurities are rejected to the solidification front based on the retrograde solubilities of impurity elements in solid silicon [10]. However, the selection of metallic agents should meet some criterias [11] and some metallic solvents such as aluminum (Al), calcium (Ca), copper (Cu), iron (Fe) and tin (Sn) have been used as the impurity getter, and the detail comparisons between the effectiveness of these elements have also been illustrated by Johnston et al. [12]. Among them, Al has been extensively investigated as the advantages of non-intermetallic phases at Si-Al phase diagram and the low melting point [13–19]. It was found that this process was suitable for removing most impurities. In particular, the elements such as P and B, which could not be removed by conventional directional solidification, could be removed through this method. However, a large quantity of Al agent (more than 50 wt%) is necessary for obtaining a high impurities removal even though the solvent could be separated by electromagnetic separation method [14,16,17] resulting in massive waste of Al agent. From the cost and practicality standpoint, it is not desirable to deal with a plenty of metal solvents in any pyrometallurgical processes. Therefore, a high-efficiency solvent will be preferred from economical and practical consideration.

According to our previous study [20], a novel phase $CaAl_2Si_2$ found in MG-Si alloyed with Ca was the only phase containing P, indicating this phase had a higher affinity for P than solid silicon as well as other precipitations. The similar phenomenon was also pointed out by several researchers [21–24]. It is expected to be a new approach for P removal by forming $CaAl_2Si_2$ phase with dissolving massive P at Si-Al-Ca alloy refining. Therefore, the present study seeks to build on this by designing to form $CaAl_2Si_2$ phase according to the Si-Al-Ca ternary phase diagram, thereby strengthening the segregation of P between solid silicon and alloy melt.

In the present work, to find a high-efficiency approach for removing P from MG-Si, Si-Al-Ca alloy refining was investigated by designing to form $CaAl_2Si_2$ phase. Distribution of P between solid silicon and the liquid Si-Al-Ca alloy was adequately discussed. Moreover, to evaluate the possibility and efficiency of P removal by Si-Al-Ca alloy refining, segregation coefficients of P between solid silicon and the liquid Si-Al-Ca alloy and activity coefficients of P in solid silicon and the alloy melt at 1273–1473 K were determined.

2. Materials and methods

2.1. Materials and reagents

High purity Al powder (99.99 wt% pure), Ca piece (99.5 wt% pure), MG-Si block (impurity concentrations are listed in Table 1) and SOG-Si block (99.9995 wt% pure) were used to prepare the alloys. Alumina crucible (99.5 wt% pure) was utilized for etch experiments. For facilitating product characterization, MG-Si and SOG-Si feedstock were doped with P (99.5 wt% pure) to form MG-Si-P and SOG-Si-P alloy respectively by using an induction furnace under argon atmosphere (99.999 wt% pure). At the acid etching and acid leaching stages, distilled water and analytical grade chemicals (hydrochloric acid, hydrofluoric acid and acetic acid) were utilized to prepare all the leachants.

2.2. Experimental procedure

2.2.1. Distribution of P between solid silicon and the liquid Si-Ca-Al melt

The alloy refining process includes melting and controlling solidification of a Si-Ca-Al alloy. According to the Si-Al-Ca ternary phase diagram provided by Anglezio et al. [26], the molar ratio of Al to Ca should be maintained at 2/1 for the purpose of achieving maximum amounts of $CaAl_2Si_2$ phase. In order to obtain the primary silicon crystals during controlled cooling from above liquidus to the eutectic temperature, the silicon content should exceed 50.9 at.%. Taking into account the theoretical recovery of silicon, alloy refining was conducted on Si-Al-Ca alloys with the composition of 90 at.% Si-6.7 at.% Al-3.3 at.% Ca. The mixture of Si, Al and Ca was placed in an alumina crucible closed by an alumina lid and melted in a horizontal tube furnace under argon atmosphere. The mixture was kept at 1723 K for 6 h to ensure full homogenization and then cooled down to room temperature at the rate of 5 K/min for obtaining sample S1. In order to evaluate the effect of quenching temperature on the purity of refined silicon, the contrast experiments were carried out at 100 K below and above the eutectic temperature (1207 K) [26] with obtaining sample S2 and S3, respectively. When the temperature lowering to the specified temperature at the cooling stage, the crucible with the sample was rapidly took out of the tube furnace and immediately quenched in liquid nitrogen to avoid the loss of P [18,27].

The solidified sample was removed from the crucible and longitudinally cut into two pieces. One piece was crushed into blocks to obtain samples for morphology analysis before embedded into epoxy resin, and then polished with a 600 rpm high speed polisher. Acid etching was also conducted on the polished surface. The operating procedures of the acid etching were illustrated in detail in our previous study [20]. The other piece was crushed and ground less than 154 μm (Mesh No. 100). And then, acid leaching was performed in two steps; the first being a 1:1:2 $HCl:C_2H_4O_2:H_2O$ mixture (by volume), the second being the 1:1:2 $HCl:HF:H_2O$ mixture. Meanwhile, the liquid/sold volume ratio was fixed at 10. The temperature of every leaching step was kept at 328 K in a water bath and the time was 6 h. At the end of each experiment, the solid residues were separated by filtration, and then washed before dried.

2.2.2. Evaluation of thermodynamic properties of P between solid silicon and the Si-Ca-Al melt

Since the presence of other impurities (besides P) in the alloy can affect the thermodynamic properties of P as a result of the interactions among various impurities, high pure feedstock (SOG-Si, Al, Ca and P) and ultra-pure alumina crucible were used as the starting materials to avoid introducing other trace impurity elements. The SOG-Si-P alloy was used as silicon source at this stage. The Si-Al-Ca alloy with a composition of 80 at.% Si-13.3 at.% Al-6.7 at.% Ca was first obtained through heating up to 1723 K with the hold time of 0.25 h in an induction finance under argon atmosphere. Before determining the thermodynamics of P, a series of experiments were first carried out to determine the equilibrium time. The Si-Al-Ca alloy was heated up to 1723 K followed by one-hour dwell in the horizontal tube furnace. After that, the temperature was decreased to 1273 K at the rate of 1 K/min and then was kept at 1273 K for five dwelling times up to 4 h. After quenched by the liquid nitrogen, the solidified samples were obtained. Through the sample preparation process for morphology analysis illustrated in Section 2.2.1, Al, Ca and P concentrations in primary silicon and the alloy phase were determined by electron probe microanalysis equipped with wavelength dispersive spectrometer to assess equilibrium time. After confirming equilibrium time, the Si-Al-Ca alloys were subjected to the same heat treatment process with exception of quenching temperature specified at 1273 K, 1323 K, 1373 K, 1423 K and 1473 K.