



Segregation behavior of iron in metallurgical grade silicon during Si–Cu solvent refining



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ABSTRACT

Impurity removal from metallurgical grade silicon (MG-Si) is an important issue for solar-grade silicon production, and solvent refining is used as an effective method to purify silicon. To evaluate the purification ability of solvent refining with Si–Cu melt at 1343–1603 K, the effective segregation ratio of the main impurity element Fe between solid Si and Si–Cu melt was experimentally and theoretically determined. The results demonstrated that the effective segregation ratio of Fe increased with the increasing temperature at the range of 1343–1603 K. The corresponding removal mechanism of Fe was investigated in detail. It was found that the effective segregation ratio of Fe calculated by Scheil equation presented the same tendency with experimental results, and the theoretical calculation was more consistent with experimental results when back diffusion was considered. Moreover, Fe was found to form Si–Fe–Mn and Fe–Mn–Ti phases into Si–Cu alloy phase from MG-Si with the presence of Cu. It can be concluded that removal mechanism of Fe was not only a segregation process, but also a recombining process of impurity phase transformation.

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1. Introduction

Metallurgical grade silicon (MG-Si) is a base material in crystalline silicon solar cells [1]. Since the conversion efficiencies of solar cell are highly affected by impurity element, whose concentrations as high as 10^7 – 10^9 ppmw (parts per million weight), the concentrations of impurity must be precisely controlled [2]. To help lower costs, metallurgical methods are applied to obtain polycrystalline silicon of a required purity. These methods including slag treatment [3], vacuum refining [4], directional solidification [5], and electron beam [6] etc. It is worth noting that the impurity distribution depends on the segregation behavior of impurities in MG-Si during solidification process, which directly affects their subsequent extraction. Metallic impurities, such as iron (Fe), aluminum (Al), and calcium (Ca), are primary concentrated at the Si grain boundaries or the grain surfaces owing to their small segregation coefficients [7]. Nonmetallic impurities, namely, boron (B) and phosphorus (P), gather inside the Si grain as a result of their

large segregation coefficients [8]. To decrease the segregation coefficients of impurities in MG-Si, solvent refining is introduced to the purification of MG-Si [9]. In this process, Si recrystallization takes place from a supersaturated Si alloy, allowing retention of impurities in the remaining liquid phase. Given the low melting points and low segregation coefficients of the impurities between solid Si and alloy melt, metals such as Al [10], Fe [11], tin (Sn) [12], and copper (Cu) [13] are typically used as impurity getters.

In order to evaluate the purification ability of solvent metal during solidification, the segregation behaviors of impurity between solid Si and alloy melt were investigated. Yoshikawa and Morita studied the segregation ratios of B and P between solid Si and Si–Al melt at 1173–1373 K, and the distribution of B and P was examined by the temperature-gradient-zone melting method [14,15]. Li and Guo evaluated the segregation behaviors of metallic impurities in MG-Si during Si–Al solvent refining, and the effective segregation ratios of titanium (Ti), Fe, and manganese (Mn) were found to decrease with the increasing temperature at the range of 1023–1473 K, and the interaction of impurities in MG-Si during alloy solidification were also taken into account [16]. Hu et al. found that multiphase were formed during Si–Sn and Si–Al solvent refining process and they concentrated on the grain boundaries or

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attached to the surface of Si [17]. In our study, Cu was chosen as the impurity getter due to the low solubility of Cu in solid Si and the large difference in their densities [18]. In addition, Cu has high affinity for a wide range of elements, low activity coefficient, low effective ionic radius, reasonably low cost and forms stable inter-metallic [19]. During the solidification of Si–Cu melt, it is found that Cu prefers to precipitate at lattice imperfections and decorates them [20], and the segregation behavior of impurities in MG-Si would be transformed with the presence of Cu. Fe is one of the most common metallic impurities in Si, which could significantly affect the minority carrier lifetime of solar cells [21]. Studies have indicated that the critical concentration of Fe in Si must lower than $1 \times 10^{14}/\text{cm}^3$. For Si–Al or Si–Sn solvent refining, the impurity Fe formed Si–Fe phase is independence of the Si–Al or Si–Sn alloy phases [17], which is complicating the purification process. In the present study, it was found that Fe formed Si–Fe phase from MG-Si and embedded in the Si–Cu alloy phase during Si–Cu solvent refining process. Besides the slightly ionic radius is higher than Cu which reduces the Fe mobility in solid Si. Also the required temperature is higher due to the considerably higher melting point of Fe than Cu. Fe makes a broad range of the metastable silicides then restricts its removal to the ppmw level [22]. To enhance the removal efficiency of Fe, attentions should be paid to the segregation behavior of Fe during Si–Cu solvent refining. Although the calculation phase diagram method has been extensively used to estimate phase equilibria [23], little information about the segregation behavior of Fe is available for Si–Cu solvent refining. Hence, the thermodynamic evaluation of the segregation behavior of Fe in MG-Si during Si–Cu solvent refining process is important for the effective removal of Fe.

The main purpose of the current study is to explore the segregation behavior of Fe during Si–Cu solvent refining. In this work, MG-Si was firstly alloyed with Cu to trap Fe, and then the purified Si was recovered by acid leaching. Experimental and theoretical methods were applied to analyze the segregation ratio of Fe between solid Si and Si–Cu melt, and the corresponding mechanism was discussed.

2. Experimental

2.1. Materials and method

The raw material, MG-Si, with a purity of 99.8% was provided by Run Xiang Co., Ltd., China. Cu powders and reagent-grade HNO_3 and HF were purchased from Sinopharm Chemical Reagent Co., Ltd. The concentrations of the main impurities in raw materials are listed in Table 1. The prepared Si–Cu alloy was crushed to a size of <1 mm by jaw and roll crushers. Then, a particle size range of 74–106 μm was selected by sieving. The Si–Cu alloy powders with a particle size of 74–106 μm was used in the acid leaching experiments.

Fig. 1(a) shows a sketch of the experimental apparatus For the preparation of Si– x wt.% Cu alloy ($x = 30, 50, \text{ and } 70$), MG-Si lumps were crushed and mixed with Cu powders to form the mixture of Si– x wt.% Cu. The mixture was put in an Al_2O_3 crucible with an internal coating of Si_3N_4 . This coating not only allows easy separation of the alloy from the crucible, but also prevents impurities

from contaminating the alloy and reduces stress produced during solidification process. Then the mixture was melted in a tube furnace (total mass of ~ 100 g). For this, the mixture was heated to 1823 K at the rate of 10 K/min in an argon atmosphere, and then held for 2 h to allow for homogenization of the melt. The temperature was continuously measured using a WRe5–WRe26 thermocouple and was controlled within ± 10 K. The mixture was subsequently cooled at a rate of 5 K/min. In order to analyze the purified Si, a leaching process was required to remove the adherent Si–Cu alloy phase. The schematic illustration of the acid leaching process of the Si–Cu alloy was shown in Fig. 1(b). Leaching experiments were performed in a Teflon beaker, which was placed on a magnetic stirrer. Ten gram samples of Si–Cu alloy powders were added to 100 mL of leachant at 343 K. The mixture was stirred at 500 rpm for 8 h. The leaching experiment was done via a three-step sequential acid leaching procedure (Step 1: 2 M HNO_3 , 5 h; Step 2: 2 M $\text{HNO}_3 + 1$ M HF, 2 h; Step 3: 1 M HNO_3 , 1 h). At the end of the experiment, the solids were filtered and rinsed with distilled water until the solution was neutral and then it was dried. Solutions of both acid leaching and digestion stages were analyzed by ICP-AES to determine the concentration of the impurities in Si and Si–Cu alloy phases, respectively.

The cooling rate of Si–Cu alloy could significantly affect the segregation process of impurities during the solidification. Hence, the influence of cooling rate should be considered. In this study, the relationship between cooling rate and the eutectic (solidus) reaction temperature within Si–Cu system was investigated by different thermal analysis (DTA). As can be seen from Fig. 2, the eutectic (solidus) reaction temperature was delayed when the cooling rate was 20 K/min. However, the delay phenomenon disappeared when the cooling rates were 5 K/min and 10 K/min. These results indicated that the variation of cooling rates could influence the solidification process, and when the cooling rate decreased to less than 10 K/min, the influence of cooling rate maintained a stable state. It was verified that 5 K/min was an appropriate cooling rate.

2.2. Characterization

Concentrations of impurities in the samples were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 2000DV, PerkinElmer Inc., US). Moreover, the morphology of the specimens was detected by scanning electron microscopy and energy dispersive spectroscopy (SEM and EDS, SU70, Hitachi Co., Ltd., Japan). Finally, distributions of elements in the Si–Cu alloy were studied using an electron probe micro analyzer (EPMA, JXA-8100, Japan Electronics Co., Ltd., Japan).

3. Results and discussion

3.1. The microstructure and element distribution of Si–Cu alloy

In order to explore the distribution of Fe in Si–Cu alloy, the SEM-EDS analysis was applied. Fig. 3 shows that SEM-EDS micrographs of Si–50 wt% Cu alloy. It was found that Fe is the main impurity element in the Si–Cu alloy. The microstructure contains primary Si, Si–Cu phase and Si–Fe phase. The phase with light color is Si–Cu phase, grey color is Si–Fe phase, and dark color is primary Si, which could be identified by the EDS-mapping analysis. Although the concentration of Fe is at the range of ppmw, the solidification sequence is in accordance with the Si–Fe–Cu ternary alloy phase diagram [24]. During the solidification of Si–Cu–Fe ternary alloy, Si crystals firstly separated from the melt, because of the high melting point of Si and low solubility of Si in Cu. And then the binary eutectic Si–Fe phase formed, following the solidification of Si–Cu phase. Si would initially precipitate with Fe during the solidification

Table 1
Impurity concentrations (ppmw) in the raw materials used in the study.

Sample	Fe	Al	Ca	Ti	Mn	Ni	B	P
MG-Si	816.94	394.90	107.96	78.44	149.20	86.90	2.94	13.51
Cu	1.57	5.96	64.52	2.06	1.11	3.36	3.86	15.17

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