Leaching behavior of impurities in Ca-alloyed metallurgical grade silicon

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ABSTRACT

To explore the potential of acid leaching in purifying metallurgical grade silicon (MG-Si) for solar cell applications, the effect of silicon microstructure on its leaching behavior was systematically investigated in the present work by a combination of alloying refining with acid etching. The microstructure evolution of silicon was revealed before and after acid etching with different lixiviants. Calcium-containing precipitates were found in MG-Si after alloying with calcium. The etching results showed that the leaching behavior of impurity inclusions strongly depended on the composition of the major impurities. HCl + HF mixture was an effective lixiviant for dissolving impurity inclusions in both MG-Si and its alloy with calcium. The impurity removal efficiency of acid leaching of MG-Si was efficiently improved after alloying. Moreover, the kinetics of acid leaching of MG-Si after alloying with calcium was further discussed based on cracking shrinking model.

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1. Introduction

As mass utilization of traditional fossil fuel increased, which has led to energy crisis and environmental pollution, it is necessary for humans to find alternative energy sources. Solar energy is the most abundant among the currently known clean and renewable energy sources, hence it is regarded as having the most potential to meet energy demands. At present, silicon remains as the principal material for solar cell applications. According to the global market outlook for photovoltaics from the European Photovoltaic Industry Association, crystalline silicon is expected to maintain approximately 80% market share in production capacity of modules in the next few years (Masson et al., 2013). To meet the application standards in solar cells, the purity of silicon is required to reach 99.9999%. Converting metallurgical grade silicon (MG-Si, purity 99%) into gaseous compounds followed by distillation, reduction and deposition into high-purity silicon, modified Siemens and fluidized bed reactor processes are both energy-consuming and high-risk-bearing, adding greatly to its cost. Thus, to make such cells more competitive than other sources of electricity, finding an alternative to produce solar grade silicon (SOG-Si, purity 99.9999%) in a highly economical manner is necessary.

As inexpensive and promising methods, metallurgical purification technologies, such as acid leaching (Ma et al., 2009; Sahu and Asselin, 2012), slag treatment (Cai et al., 2011; Fang et al., 2014), alloying refining (Fang et al., 2013; Morito et al., 2013), directional solidification (Ma et al., 2013; Martorano et al., 2011), plasma refining (Alemany et al., 2002; Nakamura et al., 2004) and vacuum melting (Safarian and Tangstad, 2012; Zheng et al., 2011), have been receiving more and more attention.

Acid leaching is regarded as a simple and effective method to remove metallic impurity inclusions from the grain boundaries when MG-Si lumps are crushed and ground into adequate sizes, exposing the impurities to the action of acids. In 1927, Tucker (1927) first proposed the method of acid leaching for purifying pulverized MG-Si. After that, many research groups have studied different acids under various leaching conditions. Santos et al. (1990) conducted a detailed study on purification of pulverized MG-Si by leaching with different acids (HCl, H_2SO_4, HNO_3, HF and their mixture) as a function of their concentration, particle size, temperature and duration of leaching. They indicated that hydrochloric acid can be used to achieve better results than those with H_2SO_4, HNO_3 and their mixture. Chu and Chu (1983) reported that the optimal purification result was obtained by using aqua regia ($HCl:HNO_3 = 3:1$) after 100 h of refluxing. Dietl (1983) obtained the optimal purification result by utilizing the acid mixture of hydrochloric acid and hydrofluoric acid. Afterwards, Norman et al. (1985) demonstrated that upgraded silicon with 99.9% purity can be achieved by leaching in three successive steps with aqua regia, hydrofluoric acid and hydrochloric acid, with an average particle size of 100 mesh.

However, acid leaching cannot extract non-metallic impurities, such as boron (B) and phosphorus (P) which yield relatively high segregation coefficients ($k_P = 0.35$; $k_B = 0.8$) (Trumbore, 1960) between solid silicon and liquid silicon. Generally, these impurities tend to distribute uniformly in silicon lattice. Therefore, MG-Si pretreatments before acid

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leaching are necessary, such as alloying with metal getters (Xu et al., 2013; Yoshikawa et al., 2005), slag treatment (Meteleva-Fischer et al., 2012) or a series of treatments including calcinations, quenching and addition of complex ligands (Sun et al., 2013).

Alloying refining, as a promising method for upgrading MG-Si at relatively low refining temperatures, has recently received considerable attention. The addition of calcium to silicon as a phosphorus getter has been thermodynamically verified as an effective approach by Shimpo et al. (2004). They calculated a negative value of the interaction parameter between calcium and phosphorus in molten silicon at 1723 K, making phosphorus stable in molten silicon thermodynamically, enhancing phosphorus segregation and increasing subsequent phosphorus removal efficiency by acid leaching. After that, many researchers have conducted alloying with calcium directly followed by acid leaching (Johnston and Barati, 2013; Meteleva-Fischer et al., 2013) or adding calcium to silicon compounds followed by acid leaching (Hu et al., 2013; Li et al., 2014). Johnston et al. investigated the alloying refining of MG-Si by introducing titanium and calcium as metal getters to target the purity of boron and phosphorus. Although the removal efficiency of boron slightly improved with titanium addition followed by one-step acid leaching ($HCl:HNO_3:H_2O = 3:1:1$), calcium addition significantly enhanced the extraction of phosphorus via two-step acid leaching (first step: $HCl:HNO_3:H_2O = 3:1:1$; the second step: $HCl:HNO_3:H_2SO_4:H_2O = 3:1:1:4$). Recently, Meteleva-Fischer et al. reported about MG-Si alloyed with calcium followed by acid leaching. With the addition of 5 wt.% calcium and cooling rate of 1 K/min, 99.95%–99.99% purity of silicon could be achieved through one-step leaching with 20 wt.% HF + HCl mixture, and over 99.995% purity of silicon twice. In spite of numerous investigations on acid leaching to purify MG-Si, the detailed leaching behavior of MG-Si associated with alloying refining have been rarely studied.

Hence, on the basis of the above discussion, we investigated the influence of microstructure of MG-Si on its leaching behavior by combining calcium alloying with acid etching. Moreover, the effect of calcium alloying on leaching yield of impurities and the kinetics of acid leaching of Si–Ca alloys were also further studied.

2. Materials and methods

2.1. Materials

Raw MG-Si and analytical grade calcium (99.99%) were supplied by Run Xiang Co., Ltd., China and Aladdin Co., Ltd., China, respectively. The concentrations of impurities in the as-received MG-Si are listed in Table 1. The block-shaped MG-Si feedstock was crushed into powder with an average particle size less than 5 mm. Bars of calcium were cut into pieces with 10 mm length.

Analytical grade reagents, such as hydrochloric acid (HCl), nitric acid (HNO_3) and hydrofluoric acid (HF) used in this study were purchased from Sinopharm Chemical Reagent Co., Ltd., China. HCl, HCl + HNO_3 (volume ratio = 3:1), and HCl + HF mixture (volume ratio = 1:1) were selected to remove impurities from MG-Si before and after alloying refining.

Table 1
The concentrations of typical impurities in the MG-Si. All values are in parts per million weight (ppmw).

Element	Concentration	Element	Concentration
Ca	39	Ni	157
Fe	1424	Cu	56
Al	394	Mg	1.36
Mn	289	Cr	4.1
V	103	B	8.6
Ti	109	P	35

2.2. Methods

2.2.1. Alloying

MG-Si powder was mixed with 5 wt.% calcium pieces to achieve a total weight of 30 g. The mixture was placed in an alumina crucible with an alumina lid and melted in a vertical tube furnace under argon atmosphere. Samples were heated to 1723 ± 5 K at a rate of 5 K/min, and then held for 1 hour (h) to ensure homogenization. Afterward, the ingot of MG-Si alloyed with calcium (A-MG-Si) was obtained after cooling to room temperature at a rate of 5 K/min. Furthermore, the temperature was measured by Pt-6%Rh / Pt-30%Rh thermocouples.

2.2.2. Acid etching

The study on the influence of calcium addition on purifying MG-Si with acid leaching was performed by comparing the leaching yield of MG-Si and A-MG-Si after acid leaching experiments. Prior to the acid leaching treatment, for testing the acid sensitivity of precipitation phases through revealing the evolution of the silicon microstructure before and after acid leaching using different lixiviants, the etching experiments were carried out.

The obtained ingot was longitudinally cut into two pieces. One piece was crushed into blocks to obtain analytical samples before being embedded into epoxy resin, and then polished with a 2000 rpm high speed polisher. The other piece was crushed and divided into two parts. One was sieved with a particle size of 4–8 mm, and the other with a grain size less than 160 μm. These samples would be applied to subsequent acid leaching experiments. The sample of MG-Si was also prepared with the same metallographic preparation process. Before the etching experiments, an optical microscope was utilized to mark impurity inclusion upon the polished surface of these samples. After selecting an analytical location, the microstructure of the area and the chemical composition of the impurity phases were characterized using an electron probe microanalyzer with energy dispersive X-ray spectroscopy. Finally, the marked samples were immersed into HCl (2 mol/L), HCl + HNO_3 (2 mol/L), and HCl + HF mixture (2 mol/L) at room temperature for 4 h, respectively.

2.2.3. Acid leaching

After the etching experiments, treated samples were observed by electron probe microanalyzer to assess the acid sensitivity of the precipitation phases. By comparing the acid sensitivity results, the optimal lixiviant of these samples would be determined. And then, acid leaching was carried out with optimal acids in a polytetrafluoroethylene beaker at 333 ± 2 K for up to 6 h by heating the contents over a water-bath. The concentration of H^+ in the lixiviant was maintained the same as in the etching experiments, and the liquid/solid volume ratio was fixed at 10. After the acid leaching experiments, residues were filtered and washed until neutrality was achieved by deionized water before drying, and the concentrations of impurities in the residues were tested by inductively coupled plasma mass spectrometry.

2.3. Characterization

The concentrations of impurities in MG-Si and A-MG-Si after acid leaching were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, DRC II, Perkin Elmer, US). Approximately 0.5 g of leaching residue was first dissolved in 10 ml of HF (2 mol/L) + 3 ml of HNO_3 (2 mol/L) mixture. And then, the solution was slowly evaporated to the last drop at 353 K. The residual solution was diluted with deionized water before the test. The microstructure of MG-Si and composition of the precipitates were examined by electron probe microanalyzer (EPMA, JXA-8100, Jeol Ltd., Japan) equipped with energy dispersive X-ray spectroscopy (EDS, INCAE250, Oxford, England) by using an electron beam with an accelerating voltage of 2×10^4 V and a beam current of 3×10^{-8} A.