

# Enhanced acid leaching of metallurgical grade silicon in hydrofluoric acid containing hydrogen peroxide as oxidizing agent



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## ABSTRACT

The effect of hydrogen peroxide as a novel oxidizing agent on purifying metallurgical grade silicon (MG-Si) by leaching with hydrofluoric acid was investigated as a function of temperature, leaching duration, stirring and hydrofluoric acid concentration. It was found that adding oxidizing agent resulted in enhancing the extraction of impurities from MG-Si as compared to that without oxidizing agent, especially for some non-dissolving elements in the acid like copper. After 2 h of leaching MG-Si with an acid mixture composed of 1 mol L<sup>-1</sup> hydrofluoric acid and 2 mol L<sup>-1</sup> hydrogen peroxide, the purity of MG-Si increased from 99.74 to 99.99%, which was higher than 99.97% obtained without hydrogen peroxide addition. Based on cracking shrinking model, the leaching MG-Si with the mixture was under chemical reaction control. Furthermore, to investigate the reaction mechanism on leaching MG-Si, the micro-structural evolutions of MG-Si before and after exposure to each etchants were revealed.

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## 1. Introduction

Solar cells, the direct conversion of sunlight into electricity, are rapidly growing up to be an important source of electric power under the situation of energy crisis and environmental pollution. At present, most solar cells are still made by using crystalline silicon purified by modified Siemens process or fluidized bed method (Masson et al., 2013). However, the shortcomings of those methods are complex, energy-intensive and dangerous. Owing to these problems, the necessity of finding an alternative to produce solar grade silicon (SOG-Si, purity 99.9999%) in a highly economical manner is evident. In this context, the metallurgical purification technology was proposed and has attracted increasing interest for the advantages of its low cost and level of energy consumption. This technology is generally comprised of slag treatment (Cai et al., 2011; Fang et al., 2014a), acid leaching (Lai et al., 2015; Zhang et al., 2013), directional solidification (Gan et al., 2015; Ma et al., 2013), vacuum refining (Zheng et al., 2010, 2011), etc.

Acid leaching is regarded as an essential method in purification of metallurgical grade silicon (MG-Si, 98%–99% purity). The principle of this method is that owing to most of the metallic elements preferentially segregating in the liquid phase as the silicon cools, those impurities precipitate as minor phases at the grain boundaries between small crystals when MG-Si is cast into blocks (Trumbore, 1960). The purity of upgraded silicon therefore depends on removing the impurity

precipitates. Upon grinding MG-Si into a fine powder, cracks occur mainly along the grain boundaries, exposing the precipitates on the surface of the particles. By soaking the powder in a suitable acid leaching solution, therefore, most of the impurities can be eliminated. Furthermore, one of the main advantages of this method for purifying MG-Si is that, based on a low temperature process, it not only has a lower energy and equipment requirements, but also is simple to operate.

Duo to the promising advantages, acid leaching method has been widely investigated for upgrading MG-Si to SOG-Si. Early in 1927, Tucker (1927) first proposed the method of acid leaching for preparing high purity silicon. After that, considerable effort has been made to look for effective acid leaching conditions. Santos et al. (1990) made a detailed study in purification of MG-Si by acid leaching at the conditions of particle size, leaching duration, temperature and concentration of leaching agents (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl and HF), and reported that only Fe-Si and Si-Fe-Ti phases were not removed in HCl acid, but all of them were completely dissolved by the attack with HF acid. Similar phenomenon was also demonstrated by other researchers (Fang et al., 2014b; He et al., 2012; Lai et al., 2015; Margarido et al., 1997). However, some precipitates like Si-Fe-Ca and Si-Fe-Al have a relatively lower sensitivity to the attack of HF acid as compared to other precipitates (Fang et al., 2014b). Hence, successive acid leaching (Hunt et al., 1976; Norman et al., 1985; Santos et al., 1990) or using mixed acids (Fang et al., 2014b; Lai et al., 2015; Zhang et al., 2013) was adopted for removing the precipitation phases efficiently. Although the aqua regia did not have power to remove Si-Fe, Si-Fe-Ti and Si-V-Ti (Lai et al., 2015; Zhang et al., 2013), the best result of 99.9% pure upgraded silicon was obtained by leaching in two successive steps with HCl and HF (Santos

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et al., 1990), and the satisfactory results were also achieved by using the HCl and HF mixture by Lai et al. (2015) and Fang et al. (2014b). Nevertheless, the leaching procedure of successive leaching or using mixed acids is complex and a route of high production costs. The above literature survey reveals that the effectiveness of the hydrometallurgical purification of MG-Si mainly depends on the types of acid used.

Recently, some oxidizing agents were added into acid leaching solution to enhance removing precipitates, consequently improving impurity leaching yield. Sahu and Asselin (2012) studied the effects of two different oxidizing agents ( $\text{FeCl}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) on the impurity extraction from MG-Si by leaching with HCl, and found that the addition of oxidizing agent could facilitate the impurity removal from MG-Si. A maximum of 66% Ca, 92% Cr, 27% Fe, 98% Cu, 98% Ni and 89% Zn were removed from MG-Si at the condition of 10 M HCl with 0.1 M  $\text{FeCl}_3$ . However, the Si-Fe and Si-Fe-Ti phases were not eliminated in HCl acid in the presence of the oxidizing agents. In spite of numerous investigations on upgrading MG-Si by acid leaching, the impurity removal efficiency by acid leaching was not satisfied. A more effective and low-cost acid leaching agent should be found to purify MG-Si.

The corrosive nature of ferric chloride and the slow reaction kinetics of ammonium persulfate leaching have provided incentive to seek other oxidizing agents for MG-Si purification. Hydrogen peroxide, as a strong oxidant ( $E^\circ = 1.76 \text{ V}$ ) (Chartier et al., 2008) characterizes some satisfying characters, e.g. lower cost. Most of all,  $\text{H}_2\text{O}_2$  does not introduce impurity to the upgraded silicon and shows no harm to the environment, since apart from water no other reaction products are produced during the acid leaching process. Liu et al. (2012) have verified the high efficiency in removing boron and metallic impurities by acid leaching using the HF and  $\text{H}_2\text{O}_2$  mixture, but mainly focused on seeking acid leaching conditions. For better understanding acid leaching, it is essential to investigate the reactive mechanism of leaching process and its dynamic control process.

Hence, in the present paper, the aim of this work is to explore the potential of acid leaching with  $\text{H}_2\text{O}_2$  and HF mixture in purifying MG-Si for solar cell application. The effects of stirring, temperature,  $\text{H}_2\text{O}_2$  and HF concentration and duration of acid leaching on the impurity extraction from MG-Si are investigated. Meanwhile, reaction mechanism on leaching MG-Si and its dynamic control process were also discussed.

## 2. Experiments

### 2.1. Materials and reagents

The MG-Si feedstock and analytical grade chemicals (hydrofluoric acid, hydrogen peroxide and ethylene glycol) were purchased from Run Xiang Co., Ltd., China and Sinopharm Chemical Reagent Co., Ltd., China, respectively. The concentrations of main impurities in the as-received MG-Si were given in our previous work (Lai et al., 2015). The block-shaped MG-Si was crushed, pulverized and sieved to a certain size distribution (74–154  $\mu\text{m}$ ). Distilled water and analytical grade chemicals were utilized to prepare all the leaching solutions. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) functioned as an oxidizing agent and hydrofluoric acid (HF) as a leaching agent.

### 2.2. Apparatus and experimental procedure

Leaching experiments were performed in a self-assembly experimental installation. The schematic diagram of experimental apparatus is presented in Fig. 1, which primarily comprises of a Teflon three-neck flask (250 mL), a Teflon coated mechanical stirrer, a tail-gas treatment unit, and a thermostatic water bath equipped with a thermometer. The temperature of water bath was kept constant with the temperature fluctuation maintained within  $\pm 2 \text{ K}$ .

A volume of 150 mL leaching solution was added to the flask and then heated. When the temperature rose to the required level, a charge of 15 g of MG-Si was added and stirring started. All experiments were

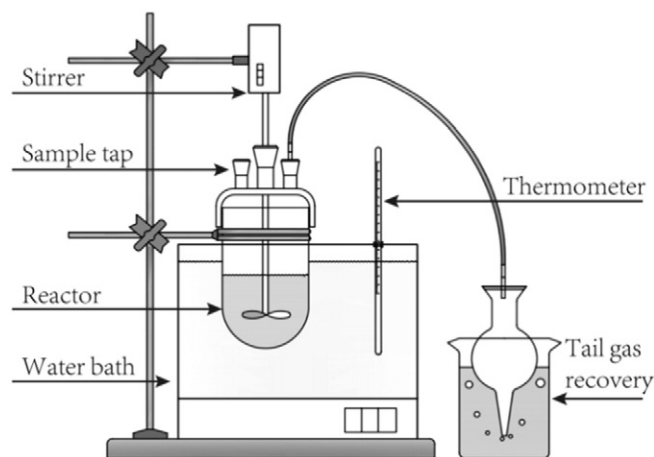


Fig. 1. Experimental installation used in MG-Si leaching experiments.

carried out with the same initial solid to liquid ratio (1:10 g/mL). At selected time intervals, aliquots were collected for determining impurity contents, and an identical volume of leaching solution was replaced in the system. The leaching residue obtained was washed thoroughly with distilled water and then dried before impurity analysis.

For testing the sensitivity of precipitation phases to various leaching solutions, the acid etchings were conducted with hydrofluoric acid alone, hydrofluoric acid plus hydrogen peroxide and the mixture of hydrofluoric acid, hydrogen peroxide and ethylene glycol. Then some comparisons were done through revealing the microstructural evolution of MG-Si before and after acid etching. The operated details of acid etching were described in my previous study (Lai et al., 2015).

### 2.3. Characterization

The concentrations of impurities in MG-Si before and after acid leaching were determined by Inductively Coupled Plasma Atomic Spectrometry (ICP-AES, Optima 2000DV, Perkin Elmer, US) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, DRC II, Perkin Elmer, US) respectively. The surface morphologies and composition of the precipitates in MG-Si before and after acid leaching were revealed 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  $2 \times 10^4 \text{ V}$  and a beam current of  $3 \times 10^{-8} \text{ A}$ .

## 3. Results and discussion

### 3.1. Effect of temperature

To investigate the effect of temperature on the purification of MG-Si, the experiments were carried out in  $1.0 \text{ mol L}^{-1}$  HF and  $2.0 \text{ mol L}^{-1}$   $\text{H}_2\text{O}_2$  mixture solution for 2 h with the temperature varying from  $25 \text{ }^\circ\text{C}$  to  $90 \text{ }^\circ\text{C}$ . The relationships between removal efficiency of representative impurities and temperature are shown in Fig. 2. The removal efficiency of some impurities, like Fe, Al, Ti and Ni is not changed with increasing temperature, indicating the effect of temperature on their removal efficiency is negligible. It should be noted that these impurities are mainly presented in the form of precipitates (Si-Fe, Si-Ti-Fe, Si-Fe-Al and Si-Al-Fe-Ni) in solid source silicon as stated in our previous report (Lai et al., 2015). And these precipitates are greatly sensitive to the HF solution alone. Hence, the precipitates will be rapidly dissolved in the case of contacting with HF acid. According to previous research, Al is difficult to leach out using the conventional acids (HF,  $\text{HNO}_3$  and HCl) or their mixture (Gribov and Zinov'ev, 2003; Kim et al., 2015; Yu et al., 2007), while the maximal extraction of Al obtained in this case is higher than 80%. On the other hand, the extractions of Ca and Cu increase slightly to maxima as the

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