Hydrometallurgy 178 (2018) 250–255

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Technical note

Removal of impurities from metallurgical grade silicon with metal assisted chemical leaching

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ARTICLE INFO

Keywords:
Metallurgical grade silicon
Silicon purification
Metal assisted chemical leaching
Micro-scale channels
Hydrometallurgy

ABSTRACT

In this study, a novel metal assisted chemical leaching (MACL) was proposed to remove impurities from metallurgical grade silicon (MG-Si). HF acid leaching, one step MACL (1-MACL, HF + $AgNO_3$) and two step MACL (2-MACL, HF + $AgNO_3$ + H_2O_2) were employed to purify MG-Si. The typical precipitates at Si grain boundaries before and after leaching were observed and analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The leaching results show that the impurities removal efficiency is 2-MACL > 1-MACL > HF acid leaching. After 2-MACL, the impurities (Fe, Al, Ca, Ti, Mn, Ni, Cu, V, Cr, Ag, B and P) concentration can be reduced from 4550.40 ppmw to 106.09 ppmw and the purity of MG-Si increased from 99.55 to 99.99%. It is notable that the introduction of micro-scale "channels" can facilitate the impurities removal when compared to solely HF leaching, especially for some non-dissolving metallic impurities like copper, calcium and aluminum. It should be noted that 2-MACL has obvious effect on the removal of non-metallic impurities B and P.

1. Introduction

Solar energy is an important source of eco-friendly and renewable energy (Ding et al., 2013), and it can be converted to electrical energy by using solar cells, which is known as photovoltaic conversion. At present, most solar cells are still made of crystalline silicon. In order to obtain the qualified solar grade silicon (SOG-Si, 99.9999%) from metallurgical grade silicon (MG-Si), the purification processes are very crucial (Goetzberger and Hebling, 2000). Siemens method, fluidized bed method and thermal decomposition of silane method are applied to purify MG-Si in the traditional industry (Ni et al., 2014; Filtvedt et al., 2010; Tejero-Ezpeleta et al., 2010). However, their high energy consumption and complex chemical reaction have seriously restricted the development of the polysilicon industry. Nowadays, there is growing interest in metallurgical route, because of its own cost and less pollution (Morita and Yoshikawa, 2011; Tan et al., 2013; Ding et al., 2012; Wei et al., 2015).

The production of solar grade silicon by the metallurgical method mainly includes slag treatment (Wu et al., 2009), hydrometallurgy (Lai et al., 2017; Zeng et al., 2012; Ma et al., 2009), secondary refining (Zhang et al., 2013a,b; Meteleva-Fischer et al., 2012a), vacuum refining (Tan et al., 2014) and directional solidification (Arafune et al., 2007). Among them, hydrometallurgical leaching purification of MG-Si should not be ignored because of its simple operation and low reaction temperature. Since Tucker (1927) reported the purification of MG-Si by acid leaching, a number of research groups have been looking for effective acid leaching conditions. Therefore, successive acid leaching (Santos et al., 1990; Zhang et al., 2013a,b; Lai et al., 2016), mixed acids leaching (Kim et al., 2015), or slag treatment followed by acid leaching (Meteleva-Fischer et al., 2012b), were adopted to remove the impurities efficiently. The leaching efficiency can be improved by using finely ground MG-Si (Dietl, 1983) or using external field (Jian et al., 2009; Xie et al., 2011) during the hydrometallurgical route. However, it is still difficult to obtain the 99.99% MG-Si by using these methods. In order to further remove impurities from MG-Si, Khalifa et al. (2012, 2013) applied vapor etching and chemical etching to introduce porous layer on the surface of MG-Si powders, the results show that this methods not only have a strong ability to remove metallic impurity from MG-Si, but

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https://doi.org/10.1016/j.hydromet.2018.05.013
Received 3 October 2017; Received in revised form 26 March 2018; Accepted 10 May 2018

also has a better extraction effect for B and P. But the difficult operation and non-ideal effect of vapor etching have limited its wide application.

Recently, metal assisted chemical etching (MACE) as a new technique that can introduce porous structure which has become a research focus (Chen and Liu, 2014; Zhang et al., 2017; Loni et al., 2011), because of its simple operation and wide application potential (Dimova-Malinovska et al., 1997; Li and Bohn, 2000; Qu et al., 2009). Combining with the hydrometallurgical refining of MG-Si technique, a simple and effective metal assisted chemical leaching (MACL) method was investigated to purify MG-Si in this paper.

2. Experiments

2.1. Experimental material and reagents

The MG-Si chunk feedstock which came from the same production batch was produced by industrial silicon company in Yunnan, China. And they were operated by hammer to some small chunks. Before experiments, two types of samples were prepared. The first sample was prepared by crushing the small MG-Si chunks into powders. The pulverized MG-Si was sieved into powders of proper sizes, between 75 and 150 μm, using a sieve shaker. The sieved powders were then cleaned using distilled water and ethanol in an ultrasonic cleaner. This sample was prepared to research for removal of impurities from MG-Si with/without the MACL. In order to check the morphologies of precipitates and study the evolution of MG-Si after leaching with different methods, the second sample was prepared by slicing the mounted MG-Si chunk into square wafers ($20 \times 20 \times 2\,mm^3$), and then polished, burnished, cleaned under the same sequence as described above. Analytical grade H_2O_2, HF, $NH_3{\cdot}H_2O$ and $AgNO_3$ were used in all the leaching solutions.

2.2. Experimental procedure and characterization

Leaching experiments were performed in a self-assembly and closed experimental installation, which was placed on a mechanical stirrer. 5 g MG-Si powders were added into 100 mL leaching solution for 2 h at 298 K. All experiments were carried out under the HF concentration of $4.6\,mol\,L^{-1}$. One step MACL (1-MACL) was performed under the HF + $AgNO_3$ solution system in dark room, and the $AgNO_3$ concentration is $0.01\,mol\,L^{-1}$. The process flow of two step MACL (2-MACL) is shown in Fig. 1, the deposition of Ag nanoparticles was firstly carried out for 60s under the condition of 1-MACL, and then $0.75\,mol\,L^{-1}$ H_2O_2 was added in HF + $AgNO_3$ solution, the leaching time was 2 h in dark room. After MACL process, the residual silver particles in the purified MG-Si powders were washed by $H_2O_2 + NH_3{\cdot}H_2O$ (1:1), and then were cleaned using deionized water several times. Subsequently, the MG-Si powders were dried and dissolved in a mixture of HF and HNO_3 (HF was added dropwise into HNO_3).

The concentrations of impurities in MG-Si powders before and after leaching were determined by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 8000, Perkin Elmer, US). Surface areas of porous silicon were tested by BET surface area analyzer (ASAP2020, Micromeritics, US). The surface of morphology and composition of the precipitates in MG-Si before and after leaching were analyzed by scanning electron microscopy (SEM, FEI QUANTA200) and electron probe microanalyzer (EPMA, JXA8230, JEOL, Japan) under the accelerating voltage of 20 kV and the beam current of 2×10^{-9} A.

3. Results and discussion

3.1. Morphologies of precipitates in MG-Si

The impurities (metallic: Fe, Al, Ca, Ti, Mn, Ni, Cu, V, Cr Ag; non-metallic: B, P) concentration in the initial metallurgical grade silicon and their segregation coefficient between solid and liquid silicon are listed in Table 1 (Trumbore, 1960; Hopkins and Rohatgi, 1986). According to Table 1, the purity of the initial MG-Si is < 99.55%, and Fe, Al, Ca, Ti, Ni and V account for > 95% in the total impurities. The existence of metallic impurities is generally divided into two forms: one is solubilized in the silicon substrate to form solid solution, and this kind of impurities are scattered in the silicon matrix. Meanwhile, the major forms of metallic impurities in the metallurgical silicon have very low segregation coefficient in the melting silicon (≪1) (He et al., 2012), which could make a variety of metallic elements gather together to form metallic impurity precipitates in the grain boundaries. Therefore, the grain boundaries contain numerous small, randomly distributed impurity phases, which relate to the convection of the MG-Si condensing process and the temperature gradient (Meteleva-Fischer et al., 2012c; Mccleverty, 1996). EPMA element mapping of typical precipitate phase in initial MG-Si is shown in Fig. 2. As shown in Fig. 2, Fe, Al and Ca can be determined as the main precipitated impurities because of their dominant concentrations (as shown in Table 1). Distribution areas of Ti and V are relatively concentrated and existed as Si-V-Ti rich phases. The typical non-metallic impurities, B and P, were not detected by EPMA in the precipitates, which can be attributed to their

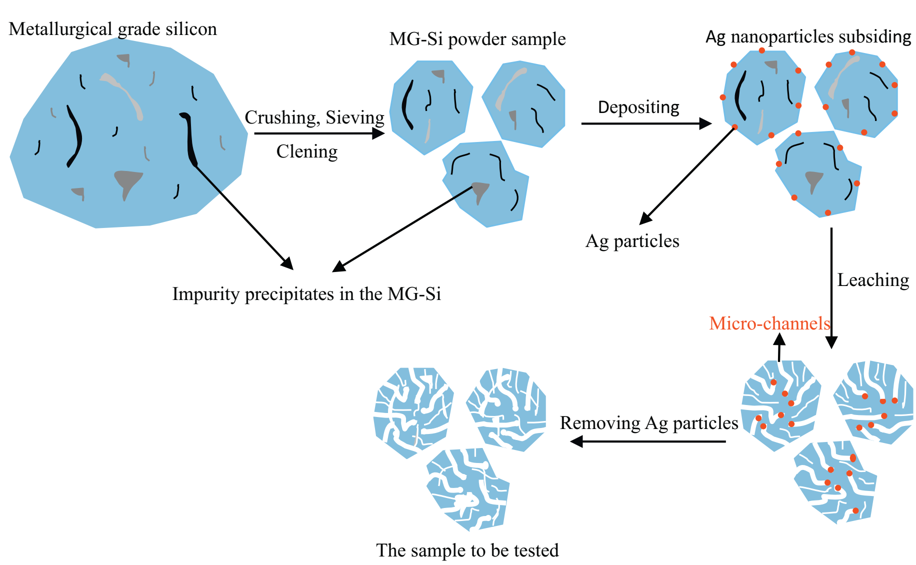

Fig. 1. Process flow of 2-MACL.