Hydrometallurgy 157 (2015) 234–238

Contents lists available at ScienceDirect

Hydrometallurgy

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

Effects of a new acid mixture on extraction of the main impurities from metallurgical grade silicon

Joonsoo Kim, Jongjin No, Sunho Choi, Jinseok Lee, Boyun Jang *

Advanced Material Laboratory, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseung-gu, Daejeon 305-343, South Korea

ARTICLE INFO

Article history:
Received 4 March 2014
Received in revised form 25 June 2015
Accepted 9 August 2015
Available online 22 August 2015

Keywords:
Metallurgical refining
Silicon
Acid leaching
Acid mixture
Extraction

ABSTRACT

A room temperature refining process using a new acidic mixture was investigated for the purification of metallurgical grade-silicon (MG-Si) with an average particle size of 617 μm. MG-Si typically contains precipitated metal impurities, such as iron (Fe), aluminum (Al) and titanium (Ti), in the triple points of grain boundaries. These metal impurities tend to concentrate within the laminar structure at grain boundaries during solidification due to their different segregation coefficients and are leached with acid at different rates because of their different reactivities with acid. The addition of acetic acid (CH_3COOH) to a conventional acid mixture composed of nitric acid (HNO_3) and hydrofluoric acid (HF) resulted in improved extraction of the main metal impurities. This new acid mixture efficiently extracted Al, which is known to be particularly difficult to remove with conventional acid leaching agents, such as hydrochloric acid (HCl), nitric acid (HNO_3), and hydrofluoric acid (HF). The recorded decreases of the Fe and Al concentrations in the material followed two distinct leaching events. The first decrease was due to the extraction of impurities located on the particle surface; the second occurred when the acid leaching time exceeded 15 h. This second leaching event may be due to the removal of metal impurities located deep in the material's pores and deep within the bulk structure of the MG-Si particles. After 25 h of leaching MG-Si with an acid mixture composed of HNO_3, HF, and CH_3COOH, the purity of the material increased from 99.74 to 99.99% with extraction efficiencies of 99.92 for Fe and 99.98% for Al and Ti.

1. Introduction

Since the last century, Si has been one of the most important materials in electronic devices. To realize this material's electrical capabilities fully, Si with a very high degree of purity is required. Generally speaking, a minimum purity of 13 N (99.99999999999%) is needed, which can only be achieved by molecular dissociation and segregation of highly purified gases such as trichlorosilane ($SiHCl_3$) or silicon tetrachloride ($SiCl_4$) (Hesse et al., 2008; Istratov et al., 2006; Khattak et al., 2001). This process is known to be very expensive as it consumes a large amount of energy and requires a lengthy processing time. Si has been used as a feedstock for the production of Si wafer-based solar cells, though the purity requirements are relatively less onerous compared to those in semiconductor manufacture. For solar cells, purities not higher than 6 N are sufficient to provide optimal efficiency in converting solar energy to electrical energy (Braga et al., 2008).

The most cost-effective and direct approach for the production of solar grade-silicon (SG-Si) is to purify and enhance MG-Si. Various investigations into methods of purifying and enhancing MG-Si to yield viable materials at lower costs have been conducted (Braga et al., 2008; Chu and Chu, 1983; Dietl, 1983; Hovel et al., 2010; Hunt et al., 1976; Jing et al., 2009; Juneja and Mukherjee, 1986; Müller et al., 2006; Peter et al., 2008; Preis et al., 2012; Safarian et al., 2012, 2013; Sakata et al., 2002; Sun et al., 2013; Tucker, 1927; Voos, 1961; Xiaddong et al., 2009; Yu et al., 2007; Zhao et al., 2011). Methods of metallurgical refining such as segregation, vacuum melting, directional solidification, and chemical leaching are potentially effective for the processing of Si feedstock for solar cells (Hovel et al., 2010; Peter et al., 2008; Preis et al., 2012; Safarian et al., 2012, 2013; Sun et al., 2013; Zhao et al., 2011). It was recently reported that p-type Czochralski (Cz)-solar cells based on Elkem Solar Silicon (ESS) feedstock (a mix of 50 wt.% Elkem Solar Silicon produced by a metallurgical processing route process and 50 wt.% "virgin" Poly-Si), which is purified by a metallurgical process such as slag treatment, leaching and solidification can achieve identical solar cell efficiencies of as found for poly-Si solar cells (Preis et al., 2012). It is worth noting that this result was realized on industrial manufacturing lines, and constitutes firm evidence of the potential of the metallurgical refining processes. As such, a significant amount of research is currently being conducted on metallurgical refining processes, among which acid leaching is one of the most commonly used and is considered a viable pretreatment in processing steps prior to the main metallurgical refining processes (Chu and Chu, 1983; Dietl, 1983; Hunt et al., 1976; Jing et al., 2009; Juneja and Mukherjee, 1986; Sakata et al., 2002; Tucker, 1927; Voos, 1961; Xiaddong et al., 2009; Yu et al., 2007).

---

* Corresponding author.
E-mail address: byjang@kier.re.kr (B. Jang).

http://dx.doi.org/10.1016/j.hydromet.2015.08.011
0304-386X/

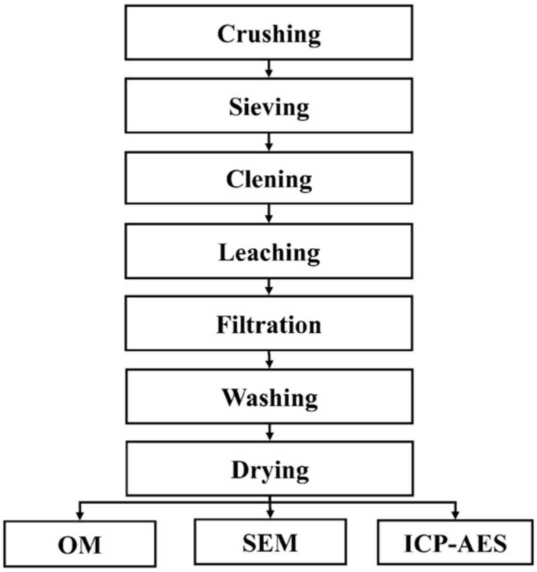

Fig. 1. Process flow chart of acid leaching.

Since the first acid leaching of Si was reported by Tucker in 1927 (Tucker, 1927), there have been many reports on refining of Si using acid. Voos reported to obtained Si suitable for microwave diodes by the treatment of pulverized MG-Si with H_2SO_4, aqua regia, HF, and other acids (Voos, 1961). Hunt et al. introduced the removal of more than 90% of the impurities in MG-Si using an average particles size of less than 50 μm by leaching with aqua regia at 75 °C for 12 h (Hunt et al., 1976). Chu et al. reported that the best results were obtained by refluxing pulverized MG-Si of undefined grain size with aqua regia, while J. Dietl et al. reported that impurities in finely ground MG-Si with a particle size of less than 20 μm were efficiently removed with mixtures of HCl and HF (Chu and Chu, 1983; Juneja and Mukherjee, 1986). According to Juneja et al., Si with a purity of 99.95% was obtained by leaching MG-Si with an average particle size of 150 μm with HF at 50 °C (Dietl, 1983). The systematic basic research of acid leaching was conducted by Sakata et al. (2002) and Yu et al. (2007). Ma Xiaodong et al. reported that particle sizes less than 100 μm were the most effective for acid leaching with HCl, HF, and HNO_3 (Xiaddong et al., 2009).

Generally speaking, smaller particle size results in higher extraction efficiency of impurities, but it brings with it a higher processing cost with the high likelihood of processing-based contamination. In the production of Si for solar cell applications, such small particles are difficult to handle in the complicated post-refining processes. Therefore, there is a limitation on particle size, which is why acid leaching is considered as a pretreatment in processing steps prior to the main metallurgical refining processes. It should be mentioned that Al is the most difficult impurity to extract by acid leaching using acids such as HCl, HNO3, and HF, especially in the case of large Si particles (Jing et al., 2009; Xiaddong et al., 2009; Yu et al., 2007).

As a pretreatment, the primary aim of acid leaching is the removal of the predominant impurities, including Fe, Al, Ca and Ti. These impurities exist in concentrations on the order of several hundred ppmw in MG-Si, while the others are present in concentrations lower than one hundred ppmw, which makes it difficult to design the refining process. If the main impurities existed in lower concentrations, the final Si purity after the primary metallurgical refining process would be enhanced. As Al is especially difficult to extract by acid leaching (Yu et al., 2007), a new acid mixture is proposed, and its effect on the extraction of the most important impurities (Fe, Ti and especially Al) is investigated.

2. Experimental procedures

The MG-Si used in this study came as chunks with average sizes of 5 – 10 cm. Two types of samples were prepared. The first sample was prepared by slicing the chunks into rectangular wafers with dimensions of 2 cm × 1 cm and thicknesses of 500 μm. These wafers were polished and subsequently cleaned with distilled water and semiconductor-grade isopropyl alcohol (IPA, purity 99.5%, Dongwoo fine-chem, Korea) in a sonicating bath. This sample was used not only to observe the microstructures of the impurities but also to compare the effects of the conventional and new acid mixtures on the extraction of impurities in a visually verifiable way. To prepare the second sample, the MG-Si chunks were crushed into powders by a jaw crusher, cone crusher, and pulverizer. The pulverized Si was sieved into powders of proper sizes, between 610 and 710 μm, using a sieve shaker. The sieved powders were then cleaned using the same sequence as described above. This second sample was prepared to research methods for practical purification of Si and to compare the extractions of the main impurities with different mixing ratios of acids.

A conventional acid mixture of HNO_3 (purity 68%, Daejung, Korea) and HF (purity 68%, Dongwoo fine-chem., Korea) was prepared in a weight ratio of 1:1. A new acid mixture was prepared with HNO_3, HF and CH_3COOH (purity 99.9%, Dongwoo fine-chem, Korea) in weight ratios of 1:1:1 and 1:1:2. For convenience, the composition of the acid mixture is expressed as $HNO_3 + HF + CH_3COOH$ (1:1:1 or 1:1:2). A stirring system with two blades in a Teflon beaker was constructed to accelerate the reaction by increasing the probability Si particles colliding during the acid leaching process. The two stirrer blades were coated with polytetrafluoroethylene.

Fig. 1 shows a flow chart of the acid leaching process. The acid mixture (100 g) was poured into the Teflon beaker and stirred at a speed of 400 rpm. Subsequently, 10 g of Si was poured into the beaker. This addition was considered the start of the recorded leaching time. All the

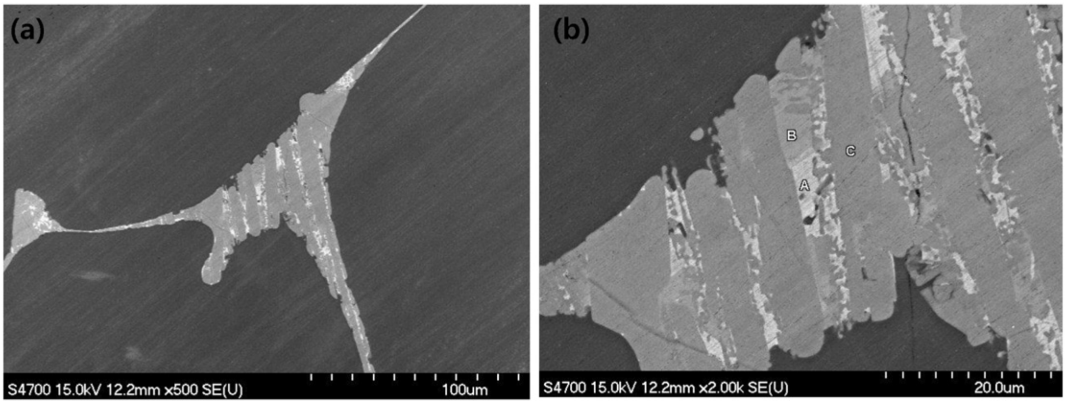

Fig. 2. (a) Surface SEM image and (b) a magnified image of the rectangular wafer prepared by slicing Si-chunk.