Hydrometallurgy 151 (2015) 84–90

Contents lists available at ScienceDirect

Hydrometallurgy

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

Density Functional Theory study of leaching efficiency of acids on Si(110) surface with adsorbed boron

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ARTICLE INFO

Article history:
Received 8 June 2014
Received in revised form 3 November 2014
Accepted 6 November 2014
Available online 15 November 2014

Keywords:
Boron removal
Hydrometallurgy
Interaction
Metallurgical grade silicon (MG-Si)
Density Functional Theory (DFT)

ABSTRACT

The Density Functional Theory (DFT)-based leaching efficiency of impurity boron from metallurgical grade silicon (MG-Si) by HCl, HNO_3, and H_2SO_4 was investigated. The boron-doped Si(110) surface was selected as the interaction interface, and respective interactions of Cl^-, NO_3^-, and SO_4^{2-} with boron were performed. The principle of boron removal by hydrometallurgy was discussed in the context of a theoretical model and a comprehensive explanation for changes in the density of states (DOS) and bond population was provided. Based on the analysis of the effect of interactions on the electronic structure and properties of the boron-doped Si(110) surface, it was found that all three types of acid ions interact strongly with boron and NO_3^- registers the strongest interaction. The analysis of the bond population of Si–B showed that these bonds are more easily broken by NO_3^- than by either Cl^- or SO_4^{2-}, and the formation of B–O bonds is promoted. Furthermore, the effects of the three types of acid agents on the removal of boron from MG-Si were discussed. Acid leaching of porous silicon was performed and the results from inductively coupled plasma (ICP) analysis indicated that the removal efficiency of boron follows the order of $HNO_3 > H_2SO_4 > HCl$. In addition, the experimental results concur with those of the calculations.

1. Introduction

Solar grade silicon (SoG-Si), with higher than 99.9999% purity, is an important material for the production of solar cells. Boron, as an impurity element, reduces the photoelectric conversion efficiency of SoG-Si by accelerating the auger recombination and reducing the lifetime of minority carriers (Osinniy et al., 2011; Wolf et al., 2002). However, boron is an obstinate impurity and is, therefore, not easily removed from metallurgical grade silicon (MG-Si). For example, directional solidification and vacuum vaporization are ineffective as removal methods owing to the large segregation coefficient of boron to silicon ($k_0 = 0.8$) and the low vapor pressure (10^{-6} Pa at 1773 K) (Martorano et al., 2011; Noriyoshi et al., 2004). The main methods which are currently used for boron removal are plasma refining (Alemany et al., 2002; Suzuki et al., 1992), slag refining (Johnston and Barati, 2010), and alloying (Gu et al., 2011). However, plasma purification uses high amounts of electricity resulting, therefore, in exorbitant processing costs (Alemany et al., 2002); slag refining requires a large amount of slag and the process must be repeated several times (Ma et al., 2013); the application of the alloy which carries the impurities into the MG-Si is also problematic (Safarian et al., 2012). Therefore, based on the aforementioned drawbacks associated with the current removal methods, a low-cost process for removing boron from MG-Si is essential.

Hydrometallurgical purification of MG-Si is an important pretreatment method. The acid leaching efficiency depends strongly on the composition and location of the impurities in the microstructure of the treated silicon. Impurity elements that are located at the grain boundaries are easily removed with hydrometallurgy. However, a previous study (Dietl, 1983) showed that acid leaching does not have a significant effect on impurities such as boron and phosphorus, which have unfavorable segregation coefficients. Moreover, Juneja and Mukherjee (1986) found that impurity boron in MG-Si exists in the form of a solid solution. Meteleva-Fischer et al. (2012) used an electron probe micro-analyzer (EPMA) to confirm the presence of boron and found that the highest concentrations are located in $FeSi_2$-based impurity phases. Meteleva-Fischer et al. (2013) also performed a large number of experiments that showed that boron removal, with a maximum efficiency of 70%, by leaching is clearly attributed to the part of boron that is dissolved in intermetallic phases on the grain boundaries. Similarly, Tang et al. (2010, 2011) investigated boron removal from MG-Si by mixed acid, HNO_3–H_2SO_4 and H_2SO_4–HF, systems. The results revealed that the boron content could be reduced from 6.89 ppmw to

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http://dx.doi.org/10.1016/j.hydromet.2014.11.002
0304-386X/

3.57 ppmw and 3.86 ppmw, respectively. The removal efficiency was, however, only about 44%. Acid leaching is ineffective against the boron that is dissolved in the silicon matrix and some pretreatment that exposes boron to the surface of silicon is, therefore, necessary. Won et al. (2011) have reported that the hydrometallurgical behavior of boron from combustion-synthesized silicon (CS-Si) is better than that of MG-Si owing to the unique microporous network structure of the CS-Si and the acid combination procedure. Furthermore, Sun et al. (2013) investigated the influence of calcination and quenching (C&Q) on boron removal and found that the many tunnels and positions generated by this process, aided the removal of boron during acid leaching. The corresponding maximum boron removal efficiency was 91.5% (from 128.0 ppmw to 10.9 ppmw). In another study (Khalifa et al., 2013), MG-Si powder was etched to form a thin, porous silicon layer, which was subsequently treated under oxygen to weaken the impurity-Si bonds. Samples were then chemically etched with dilute aqueous HF. The resulting boron content, <0.05 ppmw, represented a significant decrease in the initial, 0.7 ppmw, value.

Unfortunately, these studies did not investigate the interaction mechanism of boron removal. In addition, the existing form of boron in MG-Si is difficult to characterize since the corresponding amounts (typically 10 ppmw–40 ppmw) are below the detection limit of conventional analysis methods. Accurate simulation of the reaction via experimental methods is also very difficult and, as such, computer simulations and experiments must be combined. The interactions between boron and other species are of great significance for boron removal. Previous work (Tang et al., 2014) by the current authors investigated the interactions between boron and H^+, OH^-, and O_2 on the Si(110) surface. The results revealed that acid leaching can remove boron from MG-Si and the addition of oxygen aids in this removal.

In this study, the interactions between boron and Cl^-, NO_3^-, and SO_4^{2-} were calculated by means of the quantum chemistry calculation method based on the Density Functional Theory (DFT). The boron removal efficiency with three different types of acids, HCl, HNO_3, and H_2SO_4, is discussed. Experimental results are also compared to those of the simulations.

2. Theoretical calculations and experimental

2.1. Theoretical calculations

All calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) based on the Density Functional Theory (DFT) (Segall et al., 2002). The geometric structure, density of states, and various other properties can be predicted accurately by this program. The generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1981, 1996) functional has been used for the exchange–correlation functional and the ultrasoft pseudo-potential (Francis and Payne, 1990) was used to describe the electro-ion interactions. GGA provides a better overall description of the electronic subsystem than the local-density approximation (LDA) (Ceperley and Alder, 1980) functional. In addition, the spin-polarization of the system was ignored in the calculation. The accuracy of the energy convergence is better than 2×10^{-5} eV/atom, the electronic structure is minimized in all bands/EDFT, and the quality k-point separation is 0.05 Å^{-1}, when the energy and charge density distributions of the system are based on convergence in the self-consistent process. The valences for the atomic configurations considered in this study are Si—$3s^23p^2$, B—$2s^22p^1$, Cl—$3s^23p^5$, N—$2s^22p^3$, S—$3s^22p^4$, and O—$2s^22p^4$.

Geometry optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method (Head and Zerner, 1985) in order to obtain equilibrium structures. Grains grow randomly during melt growth of polycrystalline silicon (poly-Si) (Fujiwara et al., 2004). When the MG-Si is crushed, breakage occurs mainly at the grain boundaries owing to their low strength, and impurities are exposed to the surface. Moreover, the Si(110) is one of the preferred grain boundary plane orientations. In this study, the Si(110) surface was adapted by the slab super-cell methods and was then doped with impurity boron. The super-cell of the boron-doped Si(110) surface is shown in Fig. 1. Moreover, respective interactions of impurity boron with Cl^-, NO_3^-, and SO_4^{2-} on the Si(110) surface, formed the basis for calculations of the optimized work, density of states, and bond population.

2.2. Experimental

2.2.1. Materials

MG-Si kindly provided by a silicon factory in Yunnan province of China was selected as the starting raw material. Bulk MG-Si was crushed and pulverized by jaw and roll crushers, and then sieved to a size of <74 μm. The content (ppmw) of boron and other major metallic impurities was as follows: B (22.5 ± 4), Fe (6240), Al (2300), Ca (817), and Ti (574).

To expose impurity boron from the bulk to the surface, MG-Si powder was immersed in a solution of HF, then gradually added HNO_3 to it until the volume ratio of HF:HNO_3:H_2O was 4:1:20 (Limaye et al., 2006). The etching time was varied from 30 min to 6 h. The resulting porous silicon samples were rinsed in deionized water and dried at room temperature for leaching trials. Moreover, the residual mass of the porous silicon is about 89–97% of the initial bulk powder mass.

Hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3), and sulfuric acid (H_2SO_4) were all of analytical purity.

2.2.2. Leaching trials

Leaching experiments were performed in a glass that was placed in a water bath. 10 g of porous silicon powder was subsequently weighed and mixed with 200 ml, 4 mol/l HCl, HNO_3, and H_2SO_4, respectively. The solutions were continuously stirred by an agitator blade for 5 h. The temperature of the experiments was maintained at 75 °C. After the leaching was completed, the slurry was filtered and washed with deionized water, until the solution was almost neutral, and dried. The

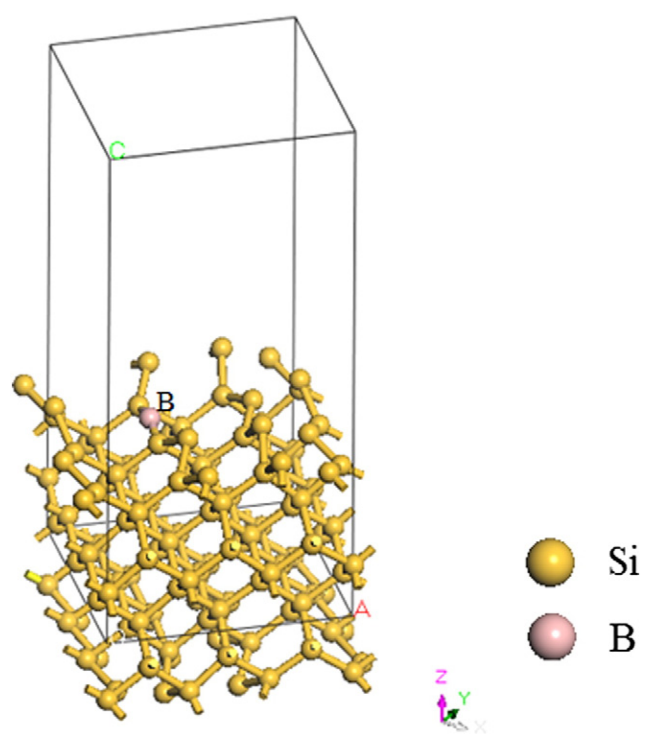

Fig. 1. Super-cell of boron-doped Si(110) surface.