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Elimination of impurities from the surface of silicon using hydrochloric and nitric acid

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ABSTRACT

Acid leaching of silicon is insufficient in order to achieve solar grade silicon. Leaching of silicon previously purified by the copper gathering method can significantly reduce amount of impurities congregated in the Cu–Si intermetallic phase during solidification process. Two samples of 50 wt% Cu–50 wt% Si alloy were solidified at 0.5 and 1.0 °C/min cooling rate. They were treated with 10 vol% HNO_3 and 5 vol% HCl and 7 vol% HNO_3. The inductively Coupled Plasma Mass Spectrometry technique was employed to measure traces of impurities before and after the treatment. It was determined that the overall impurity level in purified silicon was reduced from 5277 ppm_{wt} to 225.5 ppm_{wt}. The samples cooled at 0.5 °C/min achieved lower impurities levels in all instances while the sample leached with 10% HNO_3 produced the greatest reduction in impurity level. Scanning electron microscopy and Energy Dispersive X-Ray Spectroscopy analysis showed that the traces of Cu–Si intermetallic together with gathered impurities can be found only in the large silicon particles after the acid leaching treatment. In all instances, the surface of the silicon particles was free of impurities while Si yield was preserved at above 97%.

1. Introduction

Today's energy needs require a paradigm shift in thinking from traditional crude oil sources to new, more advanced alternative energy sources. Solar is an abundant source of energy on the planet having the potential of being the cleanest and most easily acquired alternative energy source [1]. Although there is much research being done in this field, silicon for application in solar cells still remains fairly expensive in part due to high raw materials costs associated with it.

Buonassisi et al. compared the four primary grades of silicon available today—metallurgical, commercial, solar and electronic grade where major difference is in the concentration of impurity elements [2]. Solar grade silicon (SG-Si) mostly has an each impurity element concentration less than 1 ppm or 99.999% pure Si. Davis and Rohatgi explain that even low concentrations of various metals inside silicon grain severely affect the minority carrier diffusion length, where the overall solar cell efficiency can be improved greatly by reducing the metal impurity content in silicon [3]. The raw material used to produce SG-Si is acquired from metallurgical grade silicon (MG-Si, 97–99% pure) or electronic-grade silicon (7–9 N pure). Metallurgical grade is the more cost effective of these two, and is of particular interest since it is abundant and easily acquired compared to electronic grade silicon.

Reported methods that efficiently increase the purity of MG-Si include directional solidification and zone refining [4–6], sheet-grown silicon including edge-defined Film-fed Growth (EFG), Ribbon-Grown (RG) silicon [2], reduction using carbon [7], oxidation refining [8] and acid leaching of metallurgical-grade silicon [4,9,10]. Istratov et al. have compiled a summary of the methods indicated

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above which is indicative that acid leaching is insufficient for MS-Si to achieve SG-Si since most of the impurities are trapped inside the silicon grains [11]. Santos et al. came to the similar conclusion achieving only 85% impurity removal after five hours treatment with HCl [12]. Rath and Sirtl's patent analyses show that HCl, HF, and/or H_2SO_4 acids can be used further to increase the purity of the silicon phase [13]. They propose that the leaching process occur during the crushing of the silicon in a ball mill coated with polypropylene which stops reaction between the steel and acid. Research done for Wacker Chemie AG by Dornberger introduced chemical based processes to purify and grow silicon showing that silicon impurities can be removed using acid leaching, if MG-Si was pretreated with different methods [14]. Research work performed by Mitrašinović and Utigard improved impurity reduction by alloying metallurgical silicon with copper where most of the trapped impurities in original MG-Si were gathered in Cu–Si intermetallic phase after the treatment [15,16]. The maximum impurity segregation ratio between the copper-rich phase and the silicon-phase in a Cu–Si alloy, occurred when the particle size was between 38 μm and 212 μm where the highest obstacle was removal of the solute element together with other impurities at the surface of the refined silicon. Bracht explained that Cu has high diffusion coefficient in Si lattice which allows its fast diffusion to grain boundaries or further to Si particle surface [17]. With recent advances in Si solidification methods e.g. electromagnetic continues casting [18] acid leached Si refined by copper allying have potential for steady quality satisfying for silicon solar cell industry.

The main objective of this work is to determine the feasibility of using the acid leaching technique after alloying silicon with copper as tools to improve the purity of silicon from MG-Si to SG-Si. An experimental study was designed with two different acid batches on the 50 wt% Cu–50 wt% Si alloy solidified under two cooling rates. Scanning electron microscopy and advanced chemical analyses were employed to determine distribution and concentration of solvent metal and other trace elements in pure silicon after acid leaching of Cu–Si alloy.

2. Leaching of silicon particles after separation from Cu–Si alloy

Schematic of the silicon purification procedure is given in Fig. 1. Initially silicon dendrites were separated from Cu–Si intermetallic in the 50 wt% Cu–50 wt% Si mixtures solidified under 1.0 and 0.5 °C/min cooling rates. Acid leaching was performed only on silicon reach phase (Table 1). The silicon particle size was between 53 μm and 212 μm. As an aid in the economic feasibility of using proposed process typical chemistry lab acids HCl and HNO_3 were used for removing impurities from silicon rich phase since they are not as caustic as HF and have minimal effect on silicon, reactor and lab environment. Two acid batches were synthesized with volumetric fractions 5% HCl,7% HNO_3 and 10% HNO_3, respectively. All analyses were performed at the room temperature.

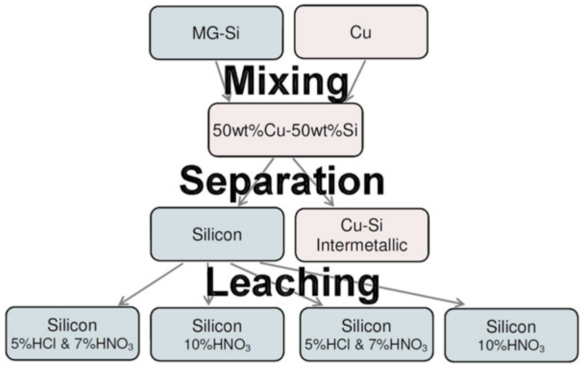

Fig. 1. Schematic of silicon purification procedure using acid leaching.

Table 1
Summary of Si rich phase of the Cu–Si alloy samples treated by different acids.

Sample	Cooling rate (°C/min)	Acid batch (vol%)	Sample weight (g)	Acid volume (ml)
10Si-ClN	1.0	5% HCl and 7% HNO_3	45.7	100
10Si-N	1.0	10% HNO_3	45.7	100
05Si-ClN	0.5	5% HCl and 7% HNO_3	51.9	100
05Si-N	0.5	10% HNO_3	52.1	100

A combination of HCl and HNO_3 acids were synthesized using deionized water, where Gastight #1050 syringe was used for chemical titration and volumetric measurements. Both acids were placed in Pyrex reactors with 10 cm inside diameter and 15 cm long chamber, and then sealed with a tight acid resistant cap. One acid reactor (5% HCl and 7% HNO_3) was filled with 20 g of silicon solidified at 1.0 °C/min, while the other 20 g silicon sample was placed into the other reactor (10% HNO_3). Remained amount of unleached sample was prepared for the ICP chemical analysis. Both reactors were then placed horizontally on a rotating mechanism where both reactors were spun simultaneously along their major axis at 120 RPMs for 1620 min. This procedure was repeated again for samples solidified at 0.5 °C/min for identical acid batches and test duration. ICP chemical analyses were performed on initial MG-Si and purified silicon after 1620 min acid leaching. Also, increase in concentration of major impurities in acid solution during leaching is monitored by extracting 2 ml sample with syringe and test tube at 60, 420, 1200, and 1620 min. All silicon and acid solution samples were analyzed in the International Plasma Laboratories in Vancouver (11620 Horseshoe Way, Richmond BC).

3. Gravimetric analyses

Room temperature gravimetric trials were carried out on refined Si samples after the 1620 min treatment in two acid batches. Mass measurements of recovered silicon samples which were placed on an analytical balance and weighed right after removal from the reactor are shown in