



Purification of metallurgical-grade silicon using zirconium as an impurity getter



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ARTICLE INFO

Article history:

Received 7 July 2016

Received in revised form 22 September 2016

Accepted 26 September 2016

Available online 30 September 2016

Keywords:

Silicon purification

Zirconium

Alloy refining

Hydrometallurgy

Metallurgical-grade silicon

ABSTRACT

Zr was employed as an impurity getter to enhance removal of impurities from MG-Si because of its strong affinity for a wide range of impurities. Different lixivants, HCl + HF, HF and aqua regia, were employed to investigate the leaching behavior of MG-Si at 348 K for 2.5 h with and without Zr addition. Typical precipitates at Si grain boundaries before and after acid leaching were observed and analyzed via scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The leaching results show that the order of efficiency of the lixivants, from highest to lowest, is HCl + HF > HF > aqua regia. HCl + HF is the optimal lixiviant for purification of MG-Si with and without Zr addition. The presence of Zr in MG-Si can significantly enhance the efficient extraction of impurities, especially P and Al, which cannot be removed efficiently using conventional hydrometallurgical technologies. The total fraction of impurities removed (Fe, Al, Ca, B, P, Zr, Ti, V, Mn, Cu and Ni) increased from 94.2 to 97.5% after HCl + HF leaching. In addition, 99.9% of the impurity getter Zr was removed, with its concentration decreasing from 50,000 ppmw to 49 ppmw after HCl + HF leaching. The residual amount of Zr in the refined Si can be further removed by directional-solidification purification because of its extremely small segregation coefficient.

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1. Introduction

Si is the main raw material for production of solar cells. As the presence of impurities in Si can greatly decrease the conversion efficiency of the solar cells, they must be eliminated in an efficient manner. The purity of Si must be at least 99.9999% (solar grade silicon or SOG-Si). The modified Siemens process can upgrade metallurgical grade silicon (MG-Si) to SOG-Si, but its high energy consumption and complex chemical reaction process contribute significantly to its high cost and environmental inefficiency. Because of its low cost, metallurgical treatment is considered a promising technology for low-cost production of high-purity Si. Researchers are constantly developing alternative methods to produce SOG-Si in ways that are more efficient, economically viable and environmentally friendly.

The idea of purifying MG-Si using one or more additives has attracted increasing attention in recent years, and is considered a promising candidate for producing SOG-Si. There are three different methods under consideration. One is addition of large amount of additives to form a solvent, which has a lower melting point than pure Si. This is known as solvent refining. Examples of solvent systems include Si-Al [1–5], Si-Fe [6,7], Si-Sn [8,9], Si-Na [10,11], Si-Cu [12,13], Si-Al-Sn [14], Si-Al-Zn [15], Si-Ga [16], etc., and combinations thereof [17]. Low energy consumption can be achieved using these solvents. The second method is addition of small amounts of additives directly to MG-Si. These additives have a strong affinity for certain impurities in MG-Si and can enhance their extraction. One example is addition of Ca [18–21] and Ti [18] as impurity getters because Ca and Ti have strong affinity for P and B, respectively, although Ti was unsuccessful as a getter for efficient removal of B [18]. The third method is a combination of the above two methods: use of solvent refining to achieve low-temperature Si purification, and addition of small amounts of additives to enhance extraction of certain impurities. In one example of our previous work, small amounts of Ti, Hf, and Zr were added to the Si-Al solvent system to enhance the removal

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of B [22–24] and a small amount of Ca was added to the Si-Sn solvent system to enhance extraction of P [25].

Although solvent refining shows a significant advantage in energy consumption, further work is needed to offer low-cost recycling of the residual solvent after Si purification. If the impurities in MG-Si can be eliminated efficiently using small amounts of one or more additives (the second method mentioned above), the Si purification process will be more efficient and economical.

Zr is employed as an impurity getter to enhance the removal of impurities from MG-Si as it has a strong affinity for a wide range of impurities. In addition, its segregation coefficient is extremely small (1.6×10^{-8} at the melting point of Si [26]) and its solubility in solid Si is negligible (less than 0.00001 ppm below 1153 K [27]), implying that it can be eliminated simultaneously with other impurities after Si purification and will not contaminate MG-Si. Our previous studies [22,23] proved that a small amount of Zr [<1100 ppm (parts per million by atom)] could significantly enhance the extraction of B using Si-Al as a solvent. However, the raw material used in our previous studies is B doped SOG-Si, we only focused on the effect of Zr on removal of B and did not consider its effect on removal of other impurities. In this study, Zr is added to MG-Si instead of Si-Al solvent to improve the Si purification process and the leaching behaviors of main impurities (Fe, Al, Ca, B, P, Zr, Ti, V, Mn, Cu and Ni) in MG-Si and Zr-alloyed MG-Si with different lixivants are investigated.

2. Experimental

MG-Si (purity $<99.411\%$) doped with 52 ppmw (parts per million by weight) B was ground into powder ($<186 \mu\text{m}$) to homogenize its composition and employed as the raw material for the subsequent experiments. The initial concentrations of the impurities in the MG-Si are listed in Table 1. The pulverized MG-Si, together with Zr pellets (purity 99.5%), was melted in a high purity and density graphite crucible (25 mm O.D., 17 mm I.D., 65 mm length) using an induction furnace to prepare a Si-5 wt% Zr alloy (the amount of Zr was 5 wt% in this study considering refining cost). As shown in Fig. 1, a Si-Mo electric resistance furnace was employed to carry out the Si purification experiments. First, the Si-5 wt% Zr alloy and the graphite crucible were held at 1773 ± 1 K for 2 h to homogenize the alloy's composition. They were then cooled to 773 K at 1.5 K/min in an Ar atmosphere (99.99%) to carry out solidification refining. For comparison, the same purification process was performed using the same amount of pulverized MG-Si without Zr addition.

After solidification refining, the samples were cut in half along their cross section. One half of each sample was ground into powder ($<186 \mu\text{m}$) by agate mortar and leached using aqua regia

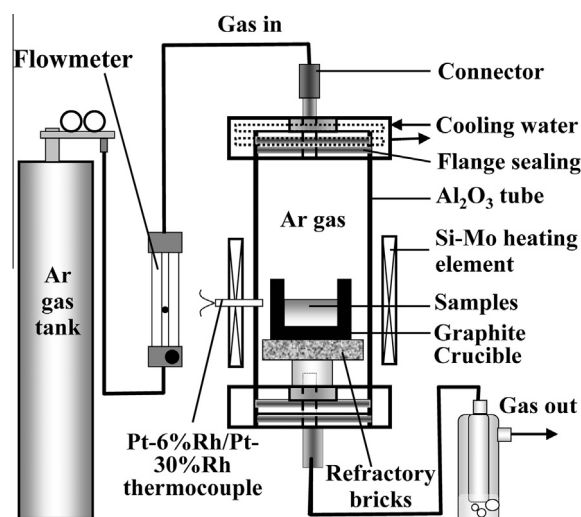


Fig. 1. Schematic of the Si-Mo electric resistance furnace.

(HCl:HNO₃ 3:1 v/v; HCl: purity 36–38%; HNO₃: purity 65–68%), HCl + HF (1:1 v/v; HF: purity 40%) and HF (purity 40%) at 348 ± 1 K for 2.5 h (100 ml Teflon beaker and shaking the beaker by hand every 30 min for stirring purpose). The ratio of solid to liquid was kept at 1:6. After acid leaching, the refined Si was dried and digested in a mixture of HNO₃ and HF (HF was added into HNO₃ as individual drops) for chemical analysis using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The other half of the sample was polished and employed for SEM observation and EDS analysis before and after acid leaching. Acid leaching used the same lixivants at the same temperature as described above.

3. Results and discussion

3.1. Morphologies of precipitates in MG-Si

The concentrations of typical impurities (Fe, Al, Ca, B, P, Zr, Ti, V, Mn, Cu and Ni) in MG-Si before acid leaching are listed in Table 1. The purity of the starting MG-Si is less than 99.41%. Fe is the dominant impurity, and others in order of concentration are Al, Ti, V, Ca, Ni, Mn, B, P, Cu and Zr. After cooling from 1773 K to 773 K at 1.5 K/min, precipitates were observed in MG-Si via SEM and their compositions analyzed via EDS. An elemental mapping analysis of a typical precipitate is shown in Fig. 2. Metal impurities were extracted into the liquid phase, and precipitated at Si grain boundaries because of their small segregation coefficients [26]. Most Ti-V

Table 1

Concentrations of impurities in MG-Si with and without Zr addition after leaching with aqua regia, HCl + HF and HF (ppmw).

Impurities	Initial MG-Si	MG-Si after leaching			MG-Si alloyed with 5 wt% Zr after leaching		
		Aqua regia	HCl + HF	HF	Aqua regia	HCl + HF	HF
Fe	3567	1910	53	34	2536	20	17
Al	1243	420	186	208	736	24	20
Ca	185	15	12	7.5	141	6.6	16
B	52	47	40	43	47	35	37
P	51	42	37	32	27	12	16
Zr	8.0	4.7	–	0.4	43,226	49	53
Ti	266	126	0.4	0.2	269	1.1	4.0
V	225	121	1.9	3.0	157	0.3	0.9
Mn	98	33	0.3	0.9	53	0.1	0.7
Cu	30	2.7	3.7	17	20	0.3	0.3
Ni	167	20	5.7	17	111	1.6	12
Total	5892	2741	340	363	47,323	150	177
Purity of Si (%)	99.411	99.726	99.966	99.964	95.268	99.985	99.982

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