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Source of boron and phosphorus impurities in the silicon wiresawing slurry and their removal by acid leaching

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ABSTRACT

Source of boron and phosphorus as the impurities in the silicon wiresawing slurry was clearly confirmed by systematical study on their elements content variation in the related materials in the cutting process. Extensive studies were concerned about the recovery of silicon particles in the wiresawing slurry. But there is little attention paid to the metal and nonmetal impurities in the slurry, especially for boron and phosphorus, which would affect the efficiency and reliability of the solar silicon cell. It was experimentally tested that for a typical steel sawing wire the boron content is about 4500 ppmw and phosphorus content is about 1000 ppmw, while in the other materials the content of the both impurities is very low. These impurities would be mixed with the silicon and silicon carbide particles after wiresawing cutting, instead of incorporating in the silicon crystal lattices. So conventional acid leaching was considered for using to effectively remove boron and phosphorus, and it was found that under optimal leaching conditions, the removal percentages of iron, boron and phosphorus were 95.50%, 82.95%, and 86.92%, respectively.

1. Introduction

Solar energy cell, as a typical cleaning and efficient energy transfer system, has become a concern in recent years due to its many prominent advantages over the traditional fossil energy utilization means [1,2]. Until 2015, the total installing capacity of photovoltaic power generation reached 55 GW around the world, rising by 36 percent over that data of one year ago [3,4]. Solar-grade silicon wafers, as the core component of solar cells, were subjunctive to a multiwire sawing process. The thickness of photovoltaic silicon wafer is usually about 0.18–0.22 mm, and the diameter of the saw wire was about 0.10–0.18 mm, so during the cutting process, the loss of the solar grade polysilicon can even reach about 50 wt%. The obtained wiresawing slurry usually contains fine particles of silicon, silicon carbide, and iron scrap, and polyethylene glycol (PEG) reagent as the suspension media, and for this mixing waste slurry it is quite worth to recycling and remanufacturing it into the solar grade silicon again in some economic and effective way [5–9].

A lot of research has concerned about the recovery of high purity silicon powders from the cutting waste. Li and Huang developed a physical sedimentation process to separate the silicon and silicon carbide particles [10,11]. The centrifugation process was also be used for recovering, for example, Liu tuned the particle surface potential combined with centrifugation, and Lin studied the effectiveness of phase transfer separation and heavy-fluid high-gravity centrifugation [12–15]. Other methods were also investigated such as filtration and froth flotation, alloy process, the electrical field and so on to separate silicon and silicon carbide particles [16–21].

Little attention has been given to the further purification of silicon separated from the wiresawing slurry. Tsai used acid treatment and electrokinetic separation to remove iron from silicon slurry [22]. They removed iron by using 1 M HNO_3 dissolvation combining with the electrokinetic separation and the removal ratio reached 90.2%, while this method takes too long time (90 h) to applicable in practice. Nishijima found that iron segments in the slurry attached to the SiC abrasive particles, so the superconducting magnetic separator was used to separate a part of the silicon carbide and most of the iron segments [23]. Lin developed a process for Si powder recovery which mainly consists of four steps: acetone washing, hydrochloric acid washing, centrifugation and hydrofluoric acid washing. The content of iron decreased from 11,600 ppm to 622 ppm after hydrochloric acid washing. On the other hand, the content of boron in the recovered Si product was 84 ppm, which is much higher than that permissible content for

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the solar-grade silicon [14]. Xing also adopted the acid leaching way to remove the iron in the silicon-rich powders. The optimal iron removal efficiency was 97%, and the content of B and P can be reduced from 21 ppm to 8 ppm and 16 ppm to 10 ppm, respectively [10].

As well known, the photoelectronic conversion of P-type polycrystalline silicon cell has high efficiency and strong anti-irradiation ability. If the substrate material of solar cells contains the elements of boron and phosphorus, the type of polycrystalline will transfer to the n-type, which will affect the photoelectronic efficiency and reliability of the solar cell significantly. In some literature, it was commonly reported that the impurities of boron and phosphorus were mixed into the wiresawing slurry [24–27]. But the source and characteristics of these two elements which can deteriorate the photoelectronic conversion properties of the polysilicon cells, have not yet been studied systematically. The two impurities level for the solar grade silicon is usually not permissible to exceed 1 ppmw [28–30]. Takeing into account of the fact that most of the metal impurities can be effectively removed by the directional solidification, but the elements of boron and phosphorus cannot be removed by pyrometallurgical method due to their large segregation coefficients which can only be effectively removed by Siemens process with high cost and complex procedures [31,32].

In the present study, the source of the phosphorous and boron would be found based on the systematical measuring firstly, and then the suitable process was developed to remove them. And we believe these two questions are greatly crucial to the recycling and reuse of the silicon contained in the waste wiresawing slurry. But where is the source of these two elements during the wiresawing process? It is still a mystery until now and there is no literature and no people that has ever mentioned or given the explain or some hints. In this study, we attempt to find the right answers to these two questions.

2. Experimental

2.1. Materials

The silicon wiresawing slurry was donated by the Liaoyang Silicon Co. Ltd, Liaoning Province of China, in which most of polyethylene glycol has been removed by washing.

2.2. Analytical techniques

The powder samples were dissolved by the mixture of nitric acid (3 mol/L) and hydrofluoric acid (2 mol/L) by taking about 3 h. The concentrations of Fe in the solution were determined by Atomic Absorption Spectrometry (AA-6600, SHIMADZU), boron and phosphorus were measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (OPTIMA 7000DV). Scanning electron microscopy (SEM) instrument (Cambridge S-360) was used to observe the morphology of the particle samples. The X-ray Fluorescence (XRF-1800 SHIMADZU) analysis was used to determine the chemical constituents of the cutting waste powders.

2.3. Pre-treatment and analysis of the wiresawing slurry

The residual polyethylene glycol (PEG) in the wiresawing slurry was further removed. The deionized water was fed to the slurry and stirred for 1 h and the mixed solution was filtrated. The filter cake was washed, dried and then ball milled for 20 min to crack the agglomerated mixed powders into the dispersed particles sufficiently.

One gram of the solid powders samples were placed in a PTFE griffin beaker and the aqueous solution of 114 ml with the concentration of 0.10 mol/L hydrofluoric acid and 0.20 mol/L nitric acid were fed to dissolve the silicon and other metals. In order to disperse the powder, the solution should be treated by ultrasonic for 20 min. Keep stirring the solution constantly until no bubbles produced which means that the dissolution reaction essentially finished. The insoluble particles were filtered washed with the deionized water for 5 times. The filtrate was collected for measuring the contents of Fe, B and P by the Inductively Coupled Plasma-Atomic Emission (ICP).

2.4. The chemical analysis of sawing wires and silicon carbide

One gram of steel saw wires samples was collected before and after silicon ingot slicing and put in a PTFE griffin beaker respectively, then though the similar procedures as that of the dissolution of wiresawing slurry to measuring the B, P and Fe contents.

Dissolved 1 g silicon carbide in the PTFE griffin beaker by the similar method which dissolve wiresawing slurry. And the ICP were used to analyze these solutions.

2.5. Heating and agitating process

The rich-silicon powder of 10 g with 100 ml deionized water was placed in a beaker. The mixed suspension was treated by ultrasonic for 20 min, in which 50 ml 2 mol/l hydrochloric acid was used at different temperature for different duration. After filtration, washing with deionized water for 5 times and drying, the silicon particle samples were obtained and sent for analysis. The removal percent defines as follows:

$$\text{Remove ratio} = \frac{10\text{ g-the content of impurity after acid leaching}}{10\text{ g}} \times 100\%$$

3. Results and discussion

3.1. The types and contents of impurities

Results show that the SiC occupies 65 percent of the mixed powders, and solar grade silicon takes 30 percent of this sample. Besides the silicon and silicon carbide, there were a variety of impurities left in the mixed powder (Fig. 1), for example, the content of iron in the sample was about 2.16 wt%. Simultaneously, boron and phosphorus were also found in the cutting waste powder, which may greatly deteriorate the photoelectronic conversion properties of the recycled silicon if used for the manufacturing of solar cell components.

3.2. Analysis of the B and P contents in the cutting silicon waste

Table 1 shows the results by XRF which suggests the elements of Fe, Mg, Al, Ni, Ca and so on consist of the main impurities, while the carbon from the SiC was not involved due to the non-detectability of light atomic weight element by XRF, as well as the boron element. The content of phosphorus was demonstrated, while the precise content must be determined by ICP analysis, as well as that of boron and it was found that boron was 75 ppmw and phosphorus was 91 ppmw in the mixed powder, as listed in tables (see Table 2).

Considering the fact that the commercial purity of solar-grade polycrystalline silicon was usually at least 99.9999 wt%, it can be inferred that contents of B and P in the silicon powders were less than 0.1 ppmw. So the impurities of boron and phosphorus were