Mechanism of enhancing B removal from Si with V addition using Al—Si as the refining solvent

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ABSTRACT

The Si purification mechanism was investigated by using Al—Si solvent with small amounts of V to enhance B removal. The results indicated that a small amount of V enhanced the removal of B from the Al—Si melt, as it formed the VB_X compound. The VB_X was determined to be VB_2 via EPMA. The solubility product of the VB_2 in the Al-43at. %Si melt at 1273 K and the Al-35at. %Si melt at 1173 K were initially measured experimentally with equilibrium technology, and were determined to be 8.15×10^{-11} (1273 K) and 5.97×10^{-12} (1173 K). The relationship between the solubility product of VB_2 and the liquidus temperature of Al—Si melt was estimated, which indicated that an excessive V addition or a lower temperature is needed to enhance the efficiency of B removal from the Al—Si melt. Based on the thermodynamic analysis, V was used as an additive in the Si purification process with the Al-35at. % Si solvent that had electromagnetic solidification. The results of the Si purification indicated that a small amount of V could enhance the B removal efficiently and VSi_2 was found in eutectic Al—Si phase along the Si crystals boundaries. The maximum removal rate of B was about 76%. The supplementary V was completely eliminated together with the B and did not contaminate the refined Si.

1. Introduction

Photovoltaic energy is seen as a solution for the foreseeable "Energy Crisis". Reducing the cost of solar grade silicon (SoG-Si) enables the production of low-cost solar cells and would popularize photovoltaic energy. SoG-Si is typically prepared using chemical method [1,2] such as the Improved Siemens Process and the Union Carbide Process. The high pollution, the high energy consumption, and the high cost of the chemical method has been one of the major obstacles in popularizing photovoltaic power generation. A low-cost, low-energy, and low-pollution technology that could manufacture SoG-Si is needed. This could be accomplished by upgrading the SoG-Si from the metallurgical grade silicon (MG-Si) via metallurgical treatments.

The ability to efficiently reduce the concentrations of impurities in the Si to the level required by the solar cells via metallurgical treatment remains difficult. The metallic impurities, such as titanium (Ti), iron (Fe) or vanadium (V), could be efficiently removed by directional solidification, because of their small segregation coefficients [3–5]. The nonmetallic impurity, phosphorus (P), could be efficiently removed by vacuum refining, because its vapor pressure is higher than that of Si [6,7]. Boron (B) cannot be removed efficiently by these above methods,

as its segregation coefficient is as large as 0.8 at 1687 K [8] and its vapor pressure is lower than that of Si [6]. Some processes, such as thermal plasma treatments [9,10] and slag treatments [11,12] have been used to remove B. A low-cost and environmentally friendly refining method is still required.

A Si purification process, using aluminum-silicon (Al—Si) solvent that are refined with electromagnetic forces [13–17], has become a promising method, due to its high efficiency, lower environmental emissions, and lower energy consumption. The segregation coefficients of the impurities become smaller in the Al—Si melt than in the molten Si, indicating that a lower refining temperature is superior for Si purification. The Si crystals are agglomerated at one end of the sample with the assistance of electromagnetic force, which indicates that the refined Si crystals could be separated from the Al—Si melt. The residual concentration of B in the refined Si remains higher than the requirement of SoG-Si (< 2.6 ppma (parts per million by atom) or 1ppmw (parts per million by weight) [18]). A method to improve the B removal efficiency with this refining process has been addressed in previous literature [19–23]. The removal of B was significantly enhanced by adding small amounts (< 1000 ppma) of transition metals (Ti [19–21], zirconium (Zr) [22] and hafnium (Hf) [23]) during the Al—Si solvent refining
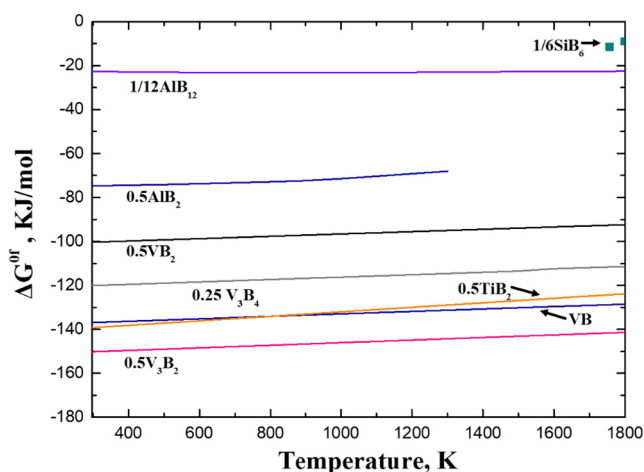
Fig. 1. The Ellingham diagram for some borides.

process (the maximum extraction ratio of B after adding Ti, Zr, and Hf is 99.4%, 97.2% and 98.2%). These transition metals (Ti, Zr, and Hf) combine with B easier than Al, so the Si and the formation of borides (TiB_2, ZrB_2, and HfB_2) cause the significant decrease of B's segregation coefficient. The additive could be simultaneously removed in the refining process, because of their small segregation coefficients (at 1687 K, Ti: 2.0×10^{-6} [8], Zr: 1.6×10^{-8} [8], Hf: 4.9×10^{-6} [23]).

This study used V to enhance the B removal from the Si during the Al−Si solvent refining process because of the following reasons: V combines with B easier than with Al and Si. The VB_X is more stable than TiB_2 when the mole ratio of V/B is larger than 1, as shown in Fig. 1. The solubility of V in the solid Si is smaller than Ti and Zr within a temperature range of 1173–1673 K [24], indicating the residual concentration V in the purified Si is smaller than Ti and Zr. The segregation coefficient of V is extremely small (at 1687 K, 4.0×10^{-6} [8]), indicating it would be removed from the Si in the Al−Si solvent refining process and would not contaminate the purified Si crystals. The formation of boride played critical role in removing B, so the solubility product of the VB_X in the Al−Si melt will be measured at 1273 K and 1173 K (Al-43at. %Si at 1273 K, Al-35at. %Si at 1173 K). The solubility product of the VB_X in the Al−Si melt of the different liquidus compositions at the corresponding liquidus temperature will be thermodynamically calculated. The Si purification will be performed by adding small amounts of V into the Al-35at. % Si melt, in order to enhance the removal of B. The mechanisms of the Si purification via the Al−Si solvent refining, with the additional V for improving B removal, will be discussed.

2. Experimental

2.1. The solubility product of V and B in Al−Si melt

An electrical resistance furnace was used to perform the thermodynamic experiments. The experiment apparatus schematic is shown in Fig. 2. The temperature of the furnace was calibrated with a B-type thermocouple. The temperature error was within ± 1 K.

A three-hole high-purity dense graphite crucible was used. Fig. 3(a) denotes the size of the crucible. Four grams of Al shot (99.999%) and bulk poly-Si (99.9999%) were added with various amounts of Si–10 wt% V and Si–1 wt% B alloy powder into each hole of the graphite crucible. The graphite crucible was kept at the constant temperature zone in the furnace. A vacuum pump (ultimate pressure: 6×10^{-2} Pa) was used to evacuate the air in the furnace tube and then to fill the tube with Ar gas (99.99%). These steps were performed at least 3 times before heating so that the samples would not be oxidized. Equilibrium was reached by holding the Al–Si-V-B melt at 1273 K and at 1173 K (Al-43at. %Si at 1273 K, Al-35at. %Si at 1173 K), in the Ar atmosphere, for

at least 12 h. The sample was then taken out of the furnace tube and placed on a copper block for quick cooling. The sample was cooled to room temperature for five minutes, and then the sample was cut lengthwise in half with the diamond-wire cutting machine. One part was polished with abrasive-paper and diamond micro-powder (particle diameter < 0.5 μm) to prepare the sample for electron probe microanalyzer (EPMA) analysis. Since the VB_X precipitate was at the bottom of the sample, taking the top half of the remaining part for chemical analysis to determine B and V contents in the Al−Si melt by employing inductively coupled plasma optical emission spectrometer (ICP-OES).

The Si–1 wt%. B alloy powder was prepared by melting the bulk poly-Si and B powder (99.9%) in an induction furnace in an Ar gas atmosphere. An agate mortar was then used to ground the alloy into powders (particle diameter < 106 μm) for compositional homogenization. The Si–10 wt%. V alloy powder was prepared with poly-Si and V chip (99.9%), following the same steps. The initial content of the B and the V in the sample were controlled by weighing the alloy powder.

2.2. Si purification using Al−Si solvent with V addition

The experiments were performed in an induction furnace with a lifting platform. The schematic of the indication furnace is provided in Fig. 4. A quartz tube was placed on the lifting platform, with a sample in it. A stepping motor was used to control the velocity and the distance of the lifting platform vertically. The position of the sample could be adjusted in the meantime. An infrared pyrometer with a triangular prism was used to measure the surface temperature of the Al−Si melt.

Ten grams of Al shot and bulk poly-Si were mixed together with various amounts of Si–1 wt%. B and Si–10 wt%. V alloy powder was placed into a high-purity dense graphite crucible, which is depicted in Fig. 3(b). The composition of these samples was set to Al-35at. %Si. The bottom of the graphite crucible was adjusted at the same level as the end of induction coils, see Fig. 4. A vacuum pump (ultimate pressure: 6×10^{-2} Pa) was used to evacuate the air in the furnace tube and then to fill the tube with Ar gas (99.99%). These steps were performed at least 3 times before heating, to ensure the samples did not oxidize. The sample was completely melted and confirmed with a triangular prism, held at 1473 K for 45 min, and then crucible was lowered to 0.56 mm/min to cool the sample slowly. The surface temperature of the Al−Si melt was recorded every 15 min during the cooling process. After the sample solidified, it was taken out and the diamond-wire cutting machine was used to cut the sample in half, lengthwise. One section was polished with abrasive-paper and diamond micro-powder (particle diameter < 0.5 μm), where it was then subjected to EPMA analysis. Separating the Si enrichment region from the remaining sections and the Si enrichment region was treated with HCl in order to remove the Al, so the Si crystals could be obtained. An agate mortar was used to ground the Si crystals into powders (particle diameter < 75 μm), which exposed the impurities. The Si powders were leached with HCl + HF (1:1 vol ratio) and aqua regia (HCl: HNO_3 = 3:1 vol ratio) at 348 K ± 1 K for 3 h, in order to move Al, V, B in the Si powders (two steps, 6 h in total). The solid/liquid ratio was 1:10 for each leaching step. The leached Si powder was then dissolved with HNO_3 + HF (HNO_3 was added into HF slowly), with the addition of a few milliliters of KF and mannitol solutions (to avoid volatilization of B), in order to determine the B, the V, and the Al contents by ICP-OES.

3. Results and discussion

3.1. The solubility product of V and B in Al−Si melt

The initial V and B contents of these samples, after equilibrium, as well as the final V and B contents of the Al−Si melt at 1273 K and 1173 K (Al-43at. %Si at 1273 K, Al-35at. %Si at 1173 K) are listed in Table 1. The B content of the Al−Si melt decreased after equilibrium,