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Short Communication

Effects of small amounts of transition metals on boron removal during electromagnetic solidification purification of silicon with Al–Si solvent

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ABSTRACT

In order to strengthen B removal during purification of Si with Al–Si solvent, small amounts (<1100 ppma) of transition metals (Hf, Zr, Ti, and Nb) were employed as additives because of their strong affinity for B. The results showed that the B removal process can be significantly improved by adding small amounts of Hf, Zr, and Ti and that Hf and Zr are more efficient for strengthening B removal than Ti or Nb. Nb had no effect on B removal. These additives could be also efficiently removed because of their extremely small segregation coefficients.

1. Introduction

In order to pursue low-cost production of Si solar cells, a promising way is to upgrade metallurgical-grade Si (MG-Si) to solar-grade Si (SoG-Si) with metallurgical treatment. However, B, an impurity in MG-Si, cannot be removed efficiently because of its low vapor pressure (lower than that of Si) [1] and large segregation coefficient (0.8 at 1687 K) [2].

Recently, a purification process using an Al–Si solvent combined with electromagnetic solidification showed outstanding results in terms of purifying Si more economically and efficiently [3,4]. Si purification could be achieved at temperatures below its melting point (1687 K). Some studies have been made to improve B removal based on this solvent-purification process [5–7]. Our research team also attempted to agglomerate Si crystals more efficiently with electromagnetic force in order to reduce the consumption of Al and also that of acid solution [8,9]. However, further efforts are still required to control the residual B in the Si to an acceptable level (<2.6 ppma or 1 ppmw) for manufacturing SoG-Si.

If B removal could be improved using small amounts of additives that have a strong affinity for B, the process would be more practical. The strong affinity of these additives for B might decrease the activity coefficient of B in the Al–Si solvent, resulting in a decrease of the segregation coefficient of B between solid Si and the Al–Si solvent. B could then be easily exposed to the leaching acid solution after grinding Si crystals, making B amenable to removal. Yoshikawa et al. [10] reported a small amount of Ti (<933 ppma) could strengthen B removal in the Al–Si solvent-purification process. Our previous study also confirmed that a small amount of Zr (<1057 ppma) was significantly responsible for strengthen B removal [11].

In order to discover which additive is more efficient for strengthen B removal, small amounts (<1100 ppma) of transition metals, Hf, Zr, Ti, and Nb, were used as additives in this study for the following reasons: (1) these elements have a stronger affinity for B than other metals (including Al and Si) based on the authors' knowledge [12,13]; (2) their segregation coefficients are extremely small [2,14], which implies that they could be simultaneously removed during solvent purification; and (3) their solubility in solid Si is extremely small [15–17]. The amount of the additives was set to less than 1100 ppma in order to keep purification costs down. Finally, the effects of these transition metals on B removal in electromagnetic solidification purification of Si with Al–Si solvent were discussed.

2. Experimental

An induction furnace (20 kHz) was employed to carry out the electromagnetic solidification purification of Si and its schematic is shown in Fig. 1. Ten grams of Al shot (99.999%) and bulk Si (99.9999%) together with different amounts of Si–M alloys (M:

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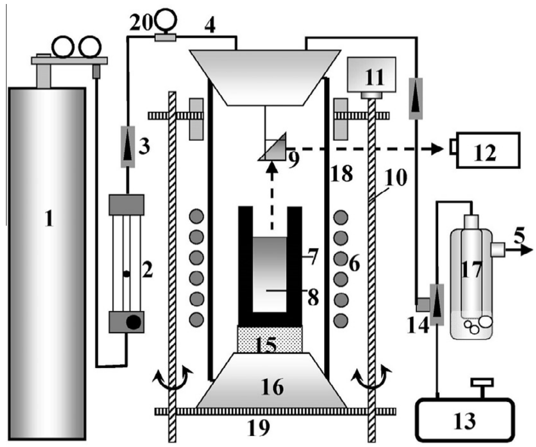

Fig. 1. Schematic of the induction furnace: 1. Ar gas tank; 2. gas flow meter; 3. two-way valve; 4. gas inlet; 5. gas outlet; 6. induction coils; 7. graphite crucible; 8. Al–Si solvent; 9. prism; 10. ball screw; 11. stepping motor; 12. infrared pyrometer; 13. vacuum pump; 14. three-way valve; 15. porous alumina holder; 16. silicone plug; 17. bubble checking; 18. quartz chamber; 19. stainless steel plate; 20. vacuum meter.

Table 1
Initial concentration of B and additives in the Al–45 at.% Si solvent and final composition of refined Si with different additives (lowering rate of 0.55 ± 0.02 mm/min; M indicates Hf, Zr, Ti, or Nb).

No.	Additive	Initial concentration of B and M, ppma (ppmw)		Final composition of refined Si, ppma (ppmw)		
		B	M	B	M	Al
1	–	153 (60)	0	62.0 (23.9)	0	317 (304)
2	Hf	153 (60)	205(1300)	13.0(5)	0.4(2.3)	439 (422)
3		153 (60)	410(2600)	12.0(4.6)	42.6(271)	496 (476)
4		153 (60)	820(5200)	6.4(2.5)	82.0(521)	526 (505)
5		153 (60)	1025 (6500)	4.6(1.8)	127(804)	435 (417)
6	Zr	153 (60)	211(700)	26.4 (10.2)	3.0(9.7)	342 (329)
7		153 (60)	422(1400)	6.3(2.4)	24.4 (79.5)	186 (179)
8		153 (60)	845(2800)	6.5(2.5)	64.6(210)	182 (176)
9		153 (60)	1057 (3500)	4.3(1.6)	225(731)	496 (476)
10	Ti	153 (60)	203(354)	61.2 (23.6)	1.2(2.1)	540 (519)
11		153 (60)	407(709)	45.1 (17.4)	1.7(3.0)	450 (432)
12		153 (60)	814(**1420**)	41.3 (15.9)	96.3(164)	570 (549)
13		153 (60)	1018 (1772)	37.1 (14.3)	248(423)	745 (716)
14	Nb	153 (60)	196(662)	65.6 (25.2)	1.7(5.6)	558 (536)
15		153 (60)	392(1324)	53.9 (20.8)	5.4(17.8)	476 (457)
16		153 (60)	785(2648)	59.2 (22.8)	5.3(17.7)	678 (652)
17		153 (60)	981(3310)	66.6 (25.6)	12.3 (40.7)	443 (426)

Hf, Zr, Ti, or Nb) and Si–1 wt% B were placed in a high-purity dense graphite crucible (25 mm O.D., 17 mm I.D., 65 mm length). The bottom of the crucible was placed level with the lower end of

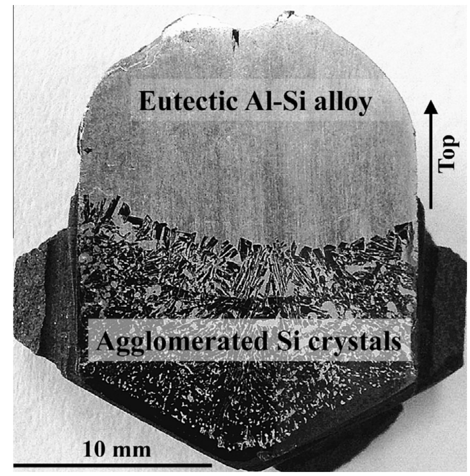

Fig. 2. A typical cross section of a Al–45 at.% Si alloy after electromagnetic solidification purification of Si.

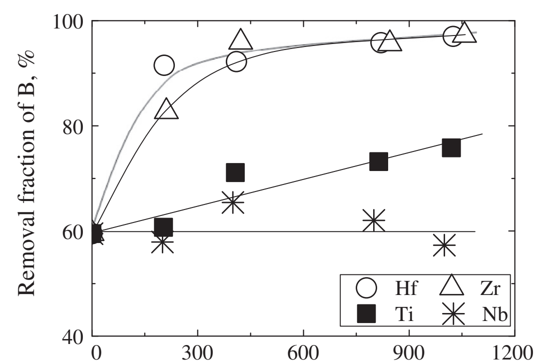

Fig. 3. B removal after electromagnetic solidification purification of Si with different additives.

the induction coils, as shown in Fig. 1. The solvent was fixed as Al–45 at% Si (the liquidus temperature is 1273 K) in order to achieve low-temperature purification. Before heating the sample, the air in the chamber of the furnace was evacuated and the chamber was refilled with Ar gas (99.99%). After melting and holding at 1473 ± 20 K for 30 min, the sample was cooled by lowering the crucible at the rate of 0.55 ± 0.02 mm/min (the corresponding cooling rate was 4.5–7.6 K/min) for solidification purification. The holding temperature of the melt was higher than its liquidus temperature (1273 K) in order to ensure complete melting and provide strong electromagnetic stirring.

After solidification, the agglomerated Si crystals were cut from the eutectic Al–Si alloy for chemical analysis. They were crushed into powders (particle diameter <186 μm) and treated with aqua regia containing H_2SO_4 ($HCl:HNO_3:H_2SO_4 = 3:1:1$) at 343 K for 6 h. The contents of B, Al, Hf, Zr, Ti, and Nb in the refined Si were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

3. Results and discussion

The initial concentration of B and M in the Al–45 at.% Si solvent and the final composition of the refined Si are listed in Table 1. The concentration of B in MG-Si has been reported to be between 13 and 130 ppma [18]. However, the initial concentration of B in the Al–Si solvent was set to 153 ppma (60 ppmw) in this study because of possible contamination from Al in an actual purification process.