

# Preparation of silicon target material by adding Al-B master alloy in directional solidification

Pengting Li<sup>1, 2,\*</sup>, Kai Wang<sup>1, 2</sup>, Shiqiang Ren<sup>1, 2</sup>, Dachuan Jiang<sup>1, 2</sup> and Yi Tan<sup>1, 2</sup>

<sup>1</sup> School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China

<sup>2</sup> Key Laboratory for Solar Energy Photovoltaic System of Liaoning Province, Dalian 116024, China

E-mail: \*ptli@dlut.edu.cn

**Abstract.** The silicon target material was prepared by adding Al-6B master alloy in directional solidification. The microstructure was characterized and the resistivity was studied in this work. The results showed that the purity of the silicon target material was more than 99.999% (5N). The resistivity was ranges from 0.002 to 0.030  $\Omega\cdot\text{cm}$  along the ingot height. It was revealed that the particles of  $\text{AlB}_2$  in Al-6B master alloy would react spontaneously and generate clusters of [B] and [Al] in molten silicon at 1723 K. After directional solidification, the content of B and Al were increasing gradually with the increase of solidified fraction. The measured values of B were in good agreement with the curve of the Scheil equation below 80% of the ingot height. The mean concentration of B was about 17.20 ppmw and the mean concentration of Al was about 8.07 ppmw after directional solidification. The measured values of Al were fitting well with the curve of values which the effective segregation coefficient was 0.00378. It was observed that B co-doped Al in directional solidification polysilicon could regulate resistivity mutually. This work provides the theoretical basis and technical support for industrial production of the silicon target material.

**Keywords:** B co-doped Al, Segregation, Resistivity, Silicon target material

## 1. Introduction

Silicon target is widely used in coating field, such as touch screen with a transparent conductive oxide film (TCO), thin film solar cells, LOW-E glass, and so on [1-3]. Silicon target as a semiconductor material, it has high hardness, wear resistance, anti-corrosion properties, and other advantages. Usually silicon target material can be prepared by directional solidification in the influence of temperature gradient [4-7], the purity of the silicon target material is required to be more than 5N, to prevent the dopant of metal impurities during the sputter coating process, and high-purity target is conducive to the uniformity of the coating. The low resistivity value is less than 0.03  $\Omega\cdot\text{cm}$ , low resistivity silicon target can ensure the conductivity of the coating. The performance of purity and resistivity are the most important factors for the use of silicon target.

During the preparation of silicon target material, group III elements such as B and Ga were used to control the resistivity. B and Ga are well-known p-type dopants. They act as acceptors in a silicon crystal. Huang et al [8] showed that the axial resistivity variation in a Ga and B co-doped Si crystal was smaller than that in simply Ga-doped Si crystal. B has a much larger equilibrium segregation coefficient ( $k_0=0.8$ ) compared to Ga. Wang et al [9] showed that using a mathematical model and

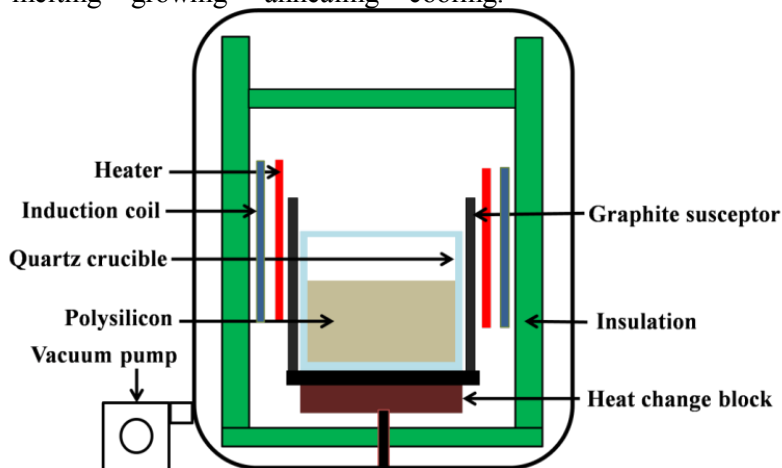


numerical analysis, that the axial resistivity distribution in silicon crystal growth can be controlled by simultaneously doping two different types of impurities, boron (B) and phosphorus (P). At present, silicon target material with high purity and low resistivity was prepared by adding Si-B master alloy in the industrial production which the resistivity could be continuously and precisely controlled. The traditional way is to add high purity Si-B master alloy, the content of B is usually 250 ppmw, and the cost of traditional adding way is higher.

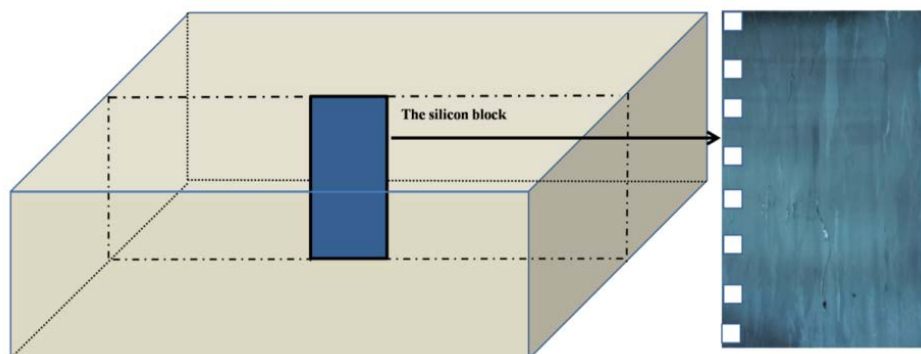
In this study, Al-6 wt. % B (Al-6B for short) master alloy was added to control the resistivity. The segregation behaviour and distribution characteristics of dopant elements were studied during the directional solidification process. This work provides the theoretical basis and technical support for industrial production of silicon target material.

## 2. Experimental procedures

Industrial directional solidification furnace (GT450) was used in this experiment, which is shown in figure 1. The produce system consists of a quartz crucible, a heat exchange block, heaters and heat insulations cage. The inner dimensions of the crucible were 1040×1040×480 mm with a silicon feedstock capacity of approximately 850 kg. Prior to processing by directional solidification under low vacuum condition, 825.44 kg silicon material was washed sufficiently with water to remove solid residues and extraneous impurities from the surface. The process of directional solidification is as follows: heating→melting→growing→annealing→cooling.



**Figure 1.** Schematic illustration of the experimental setup.



**Figure 2.** Schematic illustration of the silicon ingot and the samples.

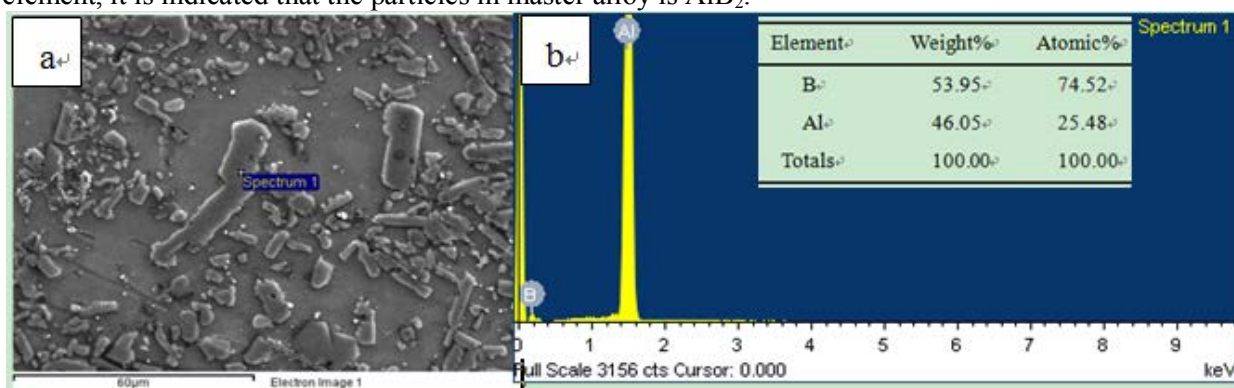
After the casting process finished, analysis of the sample was cut in the ingot as shown in the figure 2. The obtained polysilicon ingot was with a dimension of 1000 ×1000 ×357 mm. A silicon block was cut parallel along the growth direction from the middle of the ingot for observation. Eight samples

were cut from the bottom to the top of the block by diamond saw. The impurity concentrations of each sample were determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Four-point probe resistivity was performed to study the electrical performance of the whole ingot. The microstructure and composition were observed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS).

### 3. Experimental results

#### 3.1. The microstructure of the Al-6B master alloy

The microstructure of the Al-6B master alloy was analyzed by SEM and EDS, and the results are shown in figure 3. The microstructure of the Al-6B master alloy was composed a lot of rod-shaped particles. The largest size of particle is less than 60  $\mu\text{m}$ , as shown in figure 3(a). A rod-shaped area was analyzed through break-even point analysis in EDS, as shown in figure 3(b). It is observed that the main components of the master alloy are Al and B. Based on the quality percentage of each element, it is indicated that the particles in master alloy is  $\text{AlB}_2$ .



**Figure 3.** Analysis results of master alloy of Al-6B (a) Microstructure; (b) Energy spectrum analysis.

#### 3.2. Composition and resistivity analysis

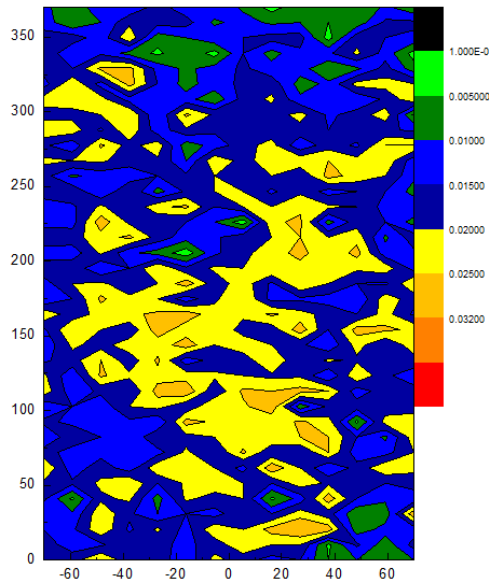
The impurity concentrations of each sample were determined by ICP-MS. The concentration of B and Al in different positions of the block are shown in table 1. It was observed that the concentrations of B and Al show an increasing trend from bottom to top of the ingot due to the segregation effect of the elements during the directional solidification process. The segregation effect of Al was more obvious compared with B in the process of directional solidification. The average concentration of B is about 17.20 ppmw in whole ingot. The concentration of Al decreases from 273.00 ppmw to 8.07 ppmw after directional solidification.

**Table 1.** Concentration of B and Al at different solidified fraction.

Solidified fraction	Concentration of B/ppmw	Concentration of Al/ppmw
0.97	18.84	64.44
0.92	20.36	11.58
0.70	16.95	3.370
0.59	16.98	1.860
0.32	15.56	1.220
0.14	16.42	1.200
0.05	15.14	1.19

Figure 4 shows the resistivity distribution of the silicon ingot. Resistivity was measured by the four point probe. The measured resistivity is P-type along the full ingot height, ranging from 0.002 to 0.030

$\Omega\cdot\text{cm}$ , which meets the performance requirement for the sputtering silicon target. The measured resistivity shows good uniformity over the ingot's surface and the change trend of resistivity from bottom to top increased firstly and then decreased. The resistivity distribution is associated with the content of element, especially for the content of B.

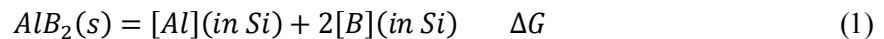


**Figure 4.** Distribution diagram of the resistivity of the sample.

## 4. Discussions

### 4.1. Thermodynamic analysis of $\text{AlB}_2$ melting reaction

From the thermodynamic point of view, only the sum of the Gibbs free energies of a series of chemical reactions is less than zero, the total chemical reaction can spontaneously react. The particle of  $\text{AlB}_2$  will melt in molten silicon at 1723K. The melting reaction produces the corresponding clusters of B and Al in molten silicon which are represented by [B] and [Al]. The possible reactions for the system are as follows:



The Gibbs free energies values of a series of reaction (2), (3) and (4) in molten silicon at 1723K are as follows:

$$\Delta G_1 = 765.71 \text{ kJ/mol} \quad (5)$$

$$\Delta G_2 = -466.809 \text{ kJ/mol} \quad (6)$$

$$\Delta G_3 = -290.614 \text{ kJ/mol}. \quad (7)$$

$$\text{Among them, } \Delta G_2 = -335000 - 76.5T(\text{J/mol}) [10] \quad (8)$$

Reaction (1) is obtained by (2) + (3) + 2(4), and the corresponding Gibbs free energies of reaction (1) is as follows:  $\Delta G = \Delta G_1 + \Delta G_2 + 2\Delta G_3 = -282.327 \text{ kJ/mol}$ . It is observed that the Gibbs free energy of reaction (1) is less than zero, so the melting reaction can spontaneously react. [B] and [Al] are may generated in molten silicon by reaction (1).

### 4.2. The segregation behaviour of B and Al

During the directional solidification process, impurities segregate at the solid-liquid interface concentrate to the liquid phase due to their lower solubility in solid than in liquid. The concentration of impurity into the solid phase during crystallization,  $C_s$  is given by the Scheil equation [11]:

$$C_s = k_{eff} C_0 (1 - f_s)^{k_{eff}-1} \quad (9)$$

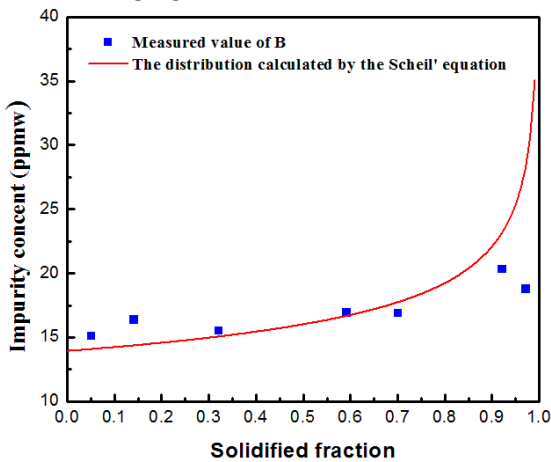
$C_0$  is the initial concentration in the liquid at the beginning of solidification.  $f_s$  is the solidified fraction.  $k_{eff}$  is the effective segregation coefficient.

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0) \exp(-v \delta / D)} \quad (10)$$

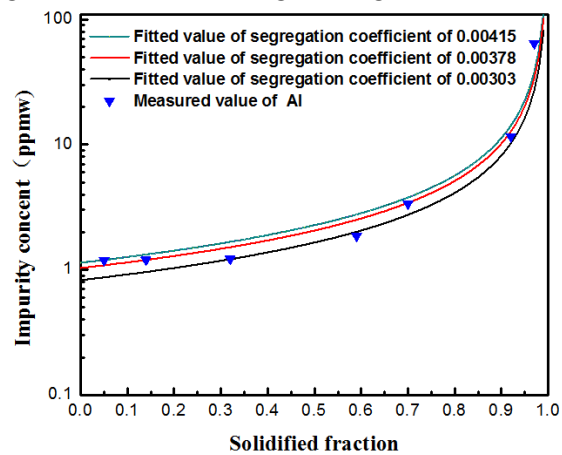
Among them,  $k_0$  is the equilibrium segregation coefficient.  $v$  is the growth rate.  $D$  ( $m^2/s$ ) is the diffusion coefficient of impurity in molten silicon.  $\delta(m)$  is the solid-liquid interface boundary layer thickness, which can be expressed as [12].

Fitted values of different effective segregation coefficient along the growth direction were calculated by Scheil equation. The results are shown in figure 5 and 6. It is found that the content of B and Al are increasing gradually with the increase of solidified fraction. The effect of segregation of B is small due to the effective segregation coefficient is 0.8 and the control of process. On the contrary, the effect of segregation of Al is obvious because the effective segregation coefficient is about  $10^{-3}$ .

As shown in figure 6, it is observed that the measured values of Al are in good agreement with the curve of the Scheil equation according to different effective segregation coefficient at different solidified fraction. Within the scope of solidified fraction of 0.3 to 0.6, the effective segregation coefficient of 0.00303 is fitting well. Within the scope of solidified fraction of 0.6 to 1.0 and 0.0 to 0.3, the effective segregation coefficient of 0.00378 is fitting well. Overall speaking, fitted values of effective segregation coefficient of 0.00378 are fitting well in the whole height of ingot.



**Figure 5.** Concentration distribution of B along the growth direction in silicon ingot.



**Figure 6.** Concentration distribution of Al along the growth direction in silicon ingot.

As a result, the distribution of Al and B can be calculated and predicted by the Scheil equation (9) and (10). Below the 80% of the ingot height, the measured values of B are in good agreement with the curve of the Scheil equation, while the measured values are lower than the value calculated by the Scheil equation in the above of 80% ingot height. The reason is that the environment change of impurity in the last solidified fraction of 20%. The values are affected by complex factors, including concentration gradient, temperature gradient and heat flow during the directional solidification process under a low vacuum condition.

#### 4.3. Effect of Doping Concentration on Resistivity

The measured resistivity along the full ingot height is range from 0.002 to 0.030  $\Omega \cdot cm$ , which the mean value is about 0.02  $\Omega \cdot cm$ . The actual doping concentration of B is about 17 ppmw. The doping concentration of B can be calculated by formulas according to the test target resistivity, just as shown below:

$$N = \frac{1.33 \times 10^{16}}{\rho} + \frac{1.082 \times 10^{17}}{\rho [1 + (54.56 \rho)^{1.105}]} \quad (11)$$

$$C = \frac{N \times W}{5 \times 10^{22} \times 28 \times 10^6} \quad (12)$$

Where  $N(\text{atom}/\text{cm}^3)$  is atomic density,  $\rho(\Omega\cdot\text{cm})$  is the resistivity,  $C(\text{ppmw})$  is the concentration,  $W$  is the atomic weight.

According to formulas (11) and (12), when the mean value of resistivity is about  $0.020 \Omega\cdot\text{cm}$ , the corresponding calculated concentration of B is about 25.01 ppmw. It is observed that the calculated doping concentration of B has a deviation of about 8 ppmw from the actual doping concentration. For the reason that the dopant contains Al and the average value of the Al is about 8.07 ppmw after DS. Al and B are in the same main groups which as the acceptor elements provide vacancy. The outermost layer of Al and B has three electrons. And these elements are presented in the form of substitution in silicon. The effect of the two elements on the resistivity is similar. As a result, the influence of this deviation on resistivity can be compensated by Al.

## 5. Conclusions

A silicon target material with high purity and low resistivity was prepared by adding Al-6B master alloy. Among them, the purity of silicon target is more than 5N, the resistivity ranges from 0.002 to  $0.030 \Omega\cdot\text{cm}$ . The content of B and Al are increasing gradually with the increase of solidified fraction. The measured values of Al were fitting well with the curve of values when the effective segregation coefficient is 0.00378. And the mean value of Al is about 8.07 ppmw. Below the 80% of the ingot height, the measured values of B are in good agreement with the curve of the Scheil equation. And the mean value of B is about 17.20 ppmw. The melting reaction of  $\text{AlB}_2$  can spontaneously react to generate clusters of [B] and [Al] in molten silicon. The outermost layer of Al and B has three electrons. These elements are presented in the form of substitution in silicon. The influence of the 8 ppmw deviation on resistivity can be compensated by Al.

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