

Determination of B impurities in silicon by inductively coupled plasma emission spectrometry

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Abstract. This article provides a method to determinate boron (B) impurity in silicon by inductively coupled plasma emission spectrometry (ICP-AES), in which the element spectral and analytical parameters were optimized. Three factors that influence testing results were discussed, including the amount of mannitol (C₆H₁₄O₆) addition, concentration of nitric acid (HNO₃) and evaporated temperature. As a result, the experimental parameters and conditions were optimized. The method of the detection limit, recovery and precision were all awarded with satisfactory results.

Introduction

As the main material for production of solar cells, 6N (99.9999%) purity solar grade polysilicon is purified from the raw material-metal silicon [1]. There are two main types of impurities in silicon, which have a serious impact on the power generation efficiency of solar cells. Due to the very low contents of these elements (usually at the ppmw level, i.e. 10⁻⁶), accurate detection of the impurities content in the solar grade poly-silicon is particularly important [2].

In recent years, method of impurity detection in silicon has been updating. Determination methods of impurity elements in the pure silicon or industrial silicon reported include inductively coupled plasma atomic emission spectrometry (ICP-AES) [3], inductively coupled plasma mass spectrometry (ICP-MS) [4], X-ray fluorescence spectrometry (XRF) [5], atomic absorption spectrometry (AAS) [6]. However, for B impurity with a low boiling point, it is easy to be lost during the silicon treatment and the testing accuracy is affected correspondingly.

In this paper, the optimum conditions for complete digestion of the silicon were studied by discussing the amount of mannitol addition, the concentration of HNO₃ and the evaporated temperature. The method developed was used for the determination of B impurity in silicon by ICP-AES, providing a basis for the accurate testing of B impurity in silicon.

Experimental

Apparatus and working conditions. ICP-AES (iCAP6300, Thermo Fisher Scientific, USA), electronic analytical balance (BSA224S-CW, Sartorius, Germany) and Heating Circulator (TopTech ME-26, JULABO, Germany). The optimal working parameters of ICP-AES are shown in Table 1.

Table 1 Optimal working parameters of ICP-AES

Source power [W]	Flow capacity of carrier gas [l/min]	Flow capacity of auxiliary gas [l/min]	Pump speed [r/min]	Analysis wavelength [nm]	Integral time [s]		Pressure of nebulizer [kPa]
					>260 nm	<260 nm	
1150	0.7	0.5	50	208.959	5	10	80

Reagents and the preparation of standard series. The reagents include hydrofluoric acid (HF, GR), nitric acid (HNO₃, GR), mannitol (C₆H₁₄O₆, GR), Ultra-pure water (18.25 MΩ·cm) and B Element Standards reserve liquid (100 µg/ml, State Nonferrous Metals and Electronic Materials Analysis and Testing Center)

Silicon sample used in the experiments: the LSSI-16-6[#] (The B content is 5.6 µg/g, detected by ICP-MS, defined as the standard test value). Based on the linear range of ICP-AES and the content of B impurity in silicon sample, the preparation of standard solution is shown in Table 2 and 5 vol% HNO₃ is used as the medium of the standard solution.

Table 2 Concentration of standards added in the preparation of calibration curve

Name	STD-1	STD-2	STD-3	STD-4	STD-5
B Concentration [µg/ml]	0.00	0.05	0.50	1.00	2.50

Digestion of the sample. A silicon sample weighing 0.2500 ± 0.0001 g was placed in a 100 ml Teflon beaker. Then 0.5 ml of 0.5 wt% mannitol solution and 3.0 ml of 49 wt% HF were added. And then 2.5 ml HNO₃ was slowly added drop by drop. After 15 min, the mixture was heated in the 50 °C oil bath until the entire sample was completely dissolved. The clear solution was heated at 90 °C oil bath to evaporate till close dryness. Then, 1.0 ml dilute HNO₃ was added and transferred to a calibrated flask, diluting to the volume of 25.0 ml with ultra-pure water.

Results and Discussions

The amount of mannitol addition. To study the influence of mannitol addition on the measured value of B impurity, the sample was accurately weighed 6 shares with the same amount. Then a concentration of 5 wt% mannitol solution was added and the amount is 0, 0.1, 0.25, 0.5, 0.8, 1.00 ml respectively. The measured value of B was shown in Fig. 1, the results showed that with the increase of mannitol addition, the value increased sharply and approached to the standard value. The curve of result appeared as platform when the amount of mannitol added was 0.5 ml. With further increase of the amount added, the measured value tended to stabilize.

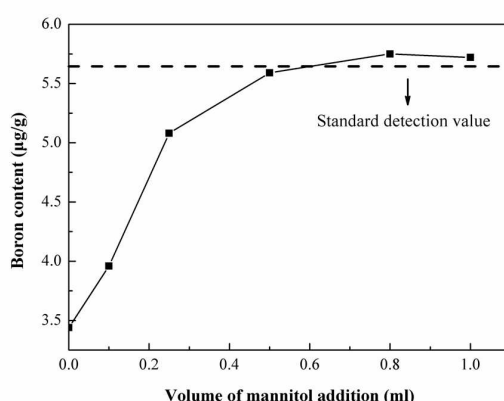


Fig. 1 Effect of mannitol amount on determination of boron

On one hand, B impurity in the silicon reacts with HF and generates BF₃ (boiling point of 173 K, gas state at room temperature), resulting in the loss of B and affecting the result of measurement. The mannitol and B can form a relatively stable complex [7], so adding an appropriate amount of mannitol can effectively inhibit the volatilization of B in the digestion process. In this article, the result is the closest to the standard value when the mannitol is added 0.5 ml at least. On the other

hand, mannitol is an organic reagent which will change the viscosity of the solution and affect the testing results. Therefore, in order to decrease the effects of the matrix to a minimum, a concentration of 0.5 wt% mannitol solution was selected with 0.5 ml.

The concentration and addition order of HNO_3 . To study the influence of HNO_3 addition on the measured value of B impurity, the sample was accurately weighed 5 shares with the same amount. Then HNO_3 solution was added respectively. The measured value of B was shown in Table 3, the results showed that the digestion time increased with the increasing of HNO_3 amount and the volatilization of B became more likely.

For the first two samples, the reaction is too severe and the system is rapidly warming and boiling when added HNO_3 solution with a concentration of 70%, resulting in serious B loss and lower detection value. For last three samples, to maintain the same amount of HNO_3 and gradually dilute HNO_3 solution by adjusting the addition order, detection value appears at the optimal range. HNO_3 solution was selected with 1 ml35%+1.5 ml70% duo to the least digestion time.

Table 3 Effect of HNO_3 amount on determination of boron

No	Volume of HNO_3	Digestion time [h]	Detection value [$\mu\text{g/g}$]	Relative error [%]
1	1 ml 70%+1 ml 70%	1.1	4.43	21.31
2	0.5 ml35%+1.75 ml70%	1.6	4.82	14.39
3	1 ml35%+1.5 ml70%	2.1	5.46	3.02
4	2 ml35%+1 ml70%	2.6	5.32	5.51
5	2 ml35%+2 ml35%	4.5	4.95	12.08

The temperature of evaporation. To study the influence of evaporation temperature (T_e) on the measured value of B impurity, the sample was accurately weighed 5 shares with the same amount. The B content was detected at the temperature of 70-150 °C respectively and spike recovery experiment was conducted. The measured value of B was shown in Fig. 2, the results showed that the digestion time decreased with the increasing of T_e . The measured value of B approached to the standard value when $T_e < 110^\circ\text{C}$. With further increase of T_e , the measured value became smaller.

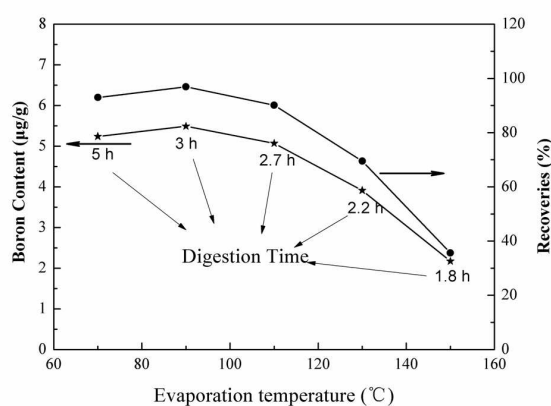


Fig. 2 Effect of evaporation temperature on determination of boron

The B loss occurs not only in the digestion stage, but also in the stage of evaporate to dryness. SiF_4 and excess HF must be evaporated completely in this stage. When T_e is too low, the efficiency will be reduced, while high T_e will make overreacting, resulting in the increasing of the B loss. A reasonable T_e makes the measured value more accurate, which can be reflected from the results of the recoveries. So 90 °C was selected as the evaporation temperature.

The detection limit, detection precision and recovery. Through continuous parallel determination of the reagent blank solution 10 times, the detection limit is obtained as 0.036 µg/ml with 3 times of standard deviation. Three same samples (LSSI-16-6 #) were accurately weighed and prepared based on the optimum parameters developed above. And then, the B content in the sample was determined, the relative standard deviation (RSD) was calculated and spike recovery experiment was conducted. The results in Table 4 show that the detection precision is satisfactory. The recoveries for the B impurity in the present method is from 95~99%, confirming no volatilization loss.

Table 4 Testing results and recoveries for the determination of boron

Sample	Found [µg/g]	Mean [µg/g]	RSD [%]	Added [µg/g]	Total found [µg/g]	Recovery [%]
1	5.38, 5.62, 5.46, 5.46, 5.52, 5.57	5.50	1.57	10.00	14.95	95.65
2	5.50, 5.52, 5.55, 5.52, 5.51, 5.49	5.52	0.18	15.00	20.06	97.24
3	5.59, 5.50, 5.56, 5.58, 5.57, 5.49	5.55	0.77	20.00	25.32	98.79

Conclusion

This article provides a method to detect B content in silicon by ICP-AES. The silicon sample was digested by the method of oil bath at atmospheric pressure in HF-HNO₃ mixed acid. Mannitol was added to inhibit the volatilization of B and the recoveries can reach more than 95%. HNO₃ solution was selected with 1 ml35%+1.5 ml 70%. 90 °C was selected as the evaporation temperature. RSD was less than 3.0% and the detection limit is 0.036 µg/ml, so the precision, accuracy of the method can meet the requirements for B detection.

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