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Determination of Trace Amounts of Boron in Polysilicon by Differential Pulse Voltammetry After Hydrofluoric Acid/Nitric Acid Treatment

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A voltammetric method for the determination of trace amounts of boron in polysilicon is proposed. The effects of several chemicals and instrumental variables were studied, and optimized operating conditions were identified. First, the sample was treated with nitric acid (HNO_3)/ hydrofluoric acid (HF) as to vaporize the silicon and stabilize boron. Thereafter, the residue boron was determined by differential pulse voltammetry, according to the monitoring the anodic peak of the complex formed between boron and Alizarin Red S (ARS) at -460 mV in ammonium acetate buffer (pH=6.5). Based on the above method, a calibration curve was established by plotting the peak current of the boron-ARS complex to the boron concentration with a linear range of 0 $\mu g \cdot mL^{-1}$-10 $\mu g \cdot mL^{-1}$. The results indicated that this method has a detection limit of 0.12 $\mu g \cdot mL^{-1}$, based on signal to ratio of 3, an average recovery of 90% ~94%, and a relative standard deviation (RSD) of 2.4%. The results obtained from this method were compared with inductively coupled plasma optical emission spectrometry (ICP-OES) method, and no statistically significant difference was found.

Keywords: Boron; Polysilicon; HNO_3/ HF treatment; Voltammetry; Alizarin Red S

1. INTRODUCTION

The photovoltaic industry has enjoyed great developments during the last decade due to the shortage of fossil fuel and the need for green technology, and most commercial photovoltaic power generation unit use polysilicon solar cells to generate electricity. The generating efficiency of solar cells is directly influenced by the identities and amounts of the impurities in polysilicon. To improve generating efficiency, polysilicon is normally doped with boron to form a P-type semiconductor. But the level of trace amounts of boron in polysilicon must be controlled very carefully in trace level, since if the boron level is too low, the conductivity of the cell is not enough, and if the boron level is too high, the conductivity is too strong and hard to control. Therefore, the determination of boron in the polysilicon materials is crucial in quality control and processing technology improvement. [1, 2].

There are many methods to detect boron content, for example, spectrophotometry [3-7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8-10], inductively coupled plasma-mass spectrometry (ICP-MS) [11], atomic absorption spectrometry (AAS) [12-14], neutron activation method [15], fluorescent spectrometry [16], chromatography [17], and so on. However, only ICP-OES and ICP-MS are suitable for the determination of boron in silicon samples. But these two methods share the same shortcomings that the testing procedures are complicated and the operation cost is normally very high.

The aim of this paper is to establish a new simple method for the determination of ppm level of boron in polysilicon. First, in the pretreatment step, polysilicon was treated with HNO_3/ HF to vaporize the silicon and to stabilize boron. Then, ARS which has strong electrochemical activity [18], was added to quickly form a complex with the residual boron [19, 20]. Thereafter, differential pulse voltammetry was applied to determine the content of boron. During the voltammetry process, the ARS-boron complex adsorbed onto the dropping mercury electrode (DME), and the anodic peak of the complex at -460 mV in ammonium acetate buffer with a pH of 6.5 was monitored to determine the boron content. The results indicated that this method enjoys the following benefits: fast turn-over, simple operation procedures, low operation cost, and high accuracy. Furthermore, the effects of several chemicals and instrumental variables have been thoroughly investigated, including digestion reagent, storage containers, ligand concentration, reaction temperature and reaction duration in the complexation step, supporting electrolyte, equilibration time of dropping mercury and scan rate.

2. EXPERIMENTAL

2.1. Instrumentation

Voltammetric measurements were performed using a polarographic analyzer of 797 VA Computrace from Metrohm Co., Ltd (Switzerland). Three-electrode system was used in this experiment with a DME as the working electrode, a Ag/AgCl with saturated KCl as the reference electrode and a platinum wire as the auxiliary electrode. A pHS-3C PH meter from Lei-Ci Co., Ltd (Shanghai, China) was utilized for PH measurement. A microwave digestion instrument from Sineo Microwave Chemistry Technology Co., Ltd (Shanghai, China) was used to volatilize silicon. An ICP-OES instrument of Advantage IRIS from Thermo Electron Corporation (America) was used for spectrophotometric determination.

2.2. Chemicals and samples

HNO_3 (68%) and HF (40%) of high purity grade were purchased from Jinhua chemical reagent Co., Ltd (Guangzhou, China). Boron (boric acid) standard solution of 1.0000 $g{\cdot}L^{-1}$ was obtained from National Analysis Center for Iron and Steel (Beijing, China). ARS, ammonium acetate and EDTA were from aladdin-reagent Co., Ltd (Shanghai, China), and these chemicals were of analytical grade. The polysilicon sample (purity is about 99.99%) was acquired from Yuantong Co., Ltd (Hangzhou, China). Deionized water with a resistivity of 18.6 MΩ was used to prepare solutions in the experiment.

2.3. Determination procedure

During the pretreatment procedure, 5.0000 g polysilicon was weighted into the polytetrafluoroethylene (PTFE) flask, followed by the addition of 4.0 mL HNO_3、10.0 mL HF and 5.0 mL deionized water. Then, the mixture was reacted in the capped PTFE flask for 30 minutes at room temperature, followed by digestion at 80 ◦C for three hours. Thereafter, solution inside the PTFE flask was heated at 90 ◦C with the cap open as to evaporate the solution to almost dryness. Finally, the PTFE flask was cooled down to room temperature, and the residual liquid in the PTFE flask was transferred to a 50.00 mL polypropylene volumetric flask and brought to 50.00 mL with the addition of deionized water.

Generally in the experiments, 100 μL of 1×10^{-3} mol·L^{-1} ARS, 100 μL of 10 mol·L $^{-1}$ ammonium acetate supporting electrolyte (PH=6.5) and 10.00 mL sample solution were pipetted into the quartz voltammetric cell, and the resulting solution was purged with nitrogen gas for 5 minutes. A new mercury drop was extruded and the stripping was initiated in the anodic direction starting from -700 mV to -300 mV by using differential pulse modulation. The instrument conditions were set at a pulse duration of 0.02 s, a pulse amplitude of 50 mV, a potential scan rate at 5 mV·s^{-1}, and an equilibration time of dropping mercury of 10 s. The sample analysis was performed in the presence of EDTA of 0.01 mol·L^{-1} in order to eliminate the interference from metal ions.

3. RESULTS AND DISCUSSION

3.1. Optimization of the digestion reagents

In this experiment, HNO_3 solution and HF solution were used for polysilicon sample digestion in a closed environment. In the pretreatment procedure, related chemical reactions are as follows:

$$3Si + 4HNO_3 + 12HF \longrightarrow 3SiF_4 + 4NO + 8H_2O$$

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

$$BF_3 + HF \longleftrightarrow HBF_4$$

After the digestion, the sample solution was heated at 90 ◦C in order to ensure SiF_4 volatize totally in great quantities and avoid the reaction of SiF_4 with water. While at temperature of 90 ◦C, boron remained in the flask in the form of H_3BO_3 and HBF_4 (the decomposition temperature of H_3BO_3

is 100 ◦C, HBF_4 is 130 ◦C). To achieve optimized digestion of the polysilicon, the amounts of the HNO_3 solution and HF solution were examined, and the results are shown in Table 1. According to the results in Table 1, the amounts of HNO_3 solution and HF solution respectively were 4 mL and 10 mL, 5 mL and 10 mL, the 5.0000 g polysilicon sample can be digested completely. In order to reduce reagent consumption and minimize blank interference, a digestion mixture containing 4 mL of HNO_3 and 10 mL of HF was chosen. Note that further experiments indicated that nitrate ions and fluoride ions derived from the digestion reagent don't interfere with the determination of boron, as discussed in section *3.10*.

Table 1. The Optimization of digestion reagent

Sample (g)	HNO_3 (mL)	HF (mL)	Digestion results
5.0000	3	8	Not completely dissolved
	3	9	Not completely dissolved
	3	10	Not completely dissolved
	4	8	Not completely dissolved
	4	9	Not completely dissolved
	4	10	Completely dissolved
	5	8	Not completely dissolved
	5	9	Not completely dissolved
	5	10	Completely dissolved

3.2. Choice of the containers used for the storage of polysilicon samples

In order to determine boron precisely and prevent the variation of boron concentration in polysilicon samples during storage, it is important to have information about the containers used for the storage. Therefore, proper containers were chosen based on the variation of boron level from a polysilicon sample containing 2.08 $\mu g \cdot g^{-1}$ of boron, containers tested including a polypropylene flask (500 mL in volume), a PTFE flask (500 mL in volume), and a glass flask (500 mL in volume). In the experiment, the boron concentration in samples stored in polypropylene flask and PTFE flask did not vary in three days, but the concentration increased for samples stored in glass flask. Since the PTFE bottle is not transparent and not easy to read the volume mark accurately, polypropylene flask is chosen for storage of sample solution. However, PTFE flask was chosen as the heating vessel during the digestion step, due to PTFE superior high temperature endurance performance.

3.3. Structure and voltammetric peak characteristic of the boron-ARS complex

ARS is an anthraquinone derivative, which has vicinal diol moieties that can easily react with boric acid to form a boron-ARS complex through mechanism as shown in Fig. 1 [21].

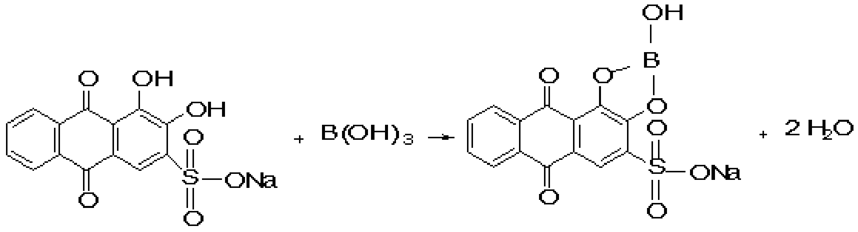


Figure 1. The complexation of ARS with boron

The ARS and boron-ARS complex both have redox nature, and the electrode reaction of the ligand is reversible and reproducible [18]. The differential pulse voltammograms of ARS (a) and boron–ARS complex (b) are shown in Fig. 2. A peak is present at −539mV (the peak current is 20.0 nA) for ARS solution with a concentration of 1×10^{-5} mol·L^{-1}, pH at 6.5 and a scan potential from -700 mV to -300 mV. After the addition of boron to the above solution, a new peak at −460mV appears (Fig. 2 (b), voltammograms of boron-ARS in the presence of 10 μg·mL^{-1} of boron, the peak current is 48.1 nA), which indicates that ARS reacts with boron to form a complex. Further investigation indicated that the intensity of the peak at -460 mV proportionally increases with the increase of boron concentration while the intensity of the peak at −539mV decreases substantially. The peak at −539 mV practically disappears when the excess boron was added to solution at concentration higher than 30 μg·mL^{-1}.

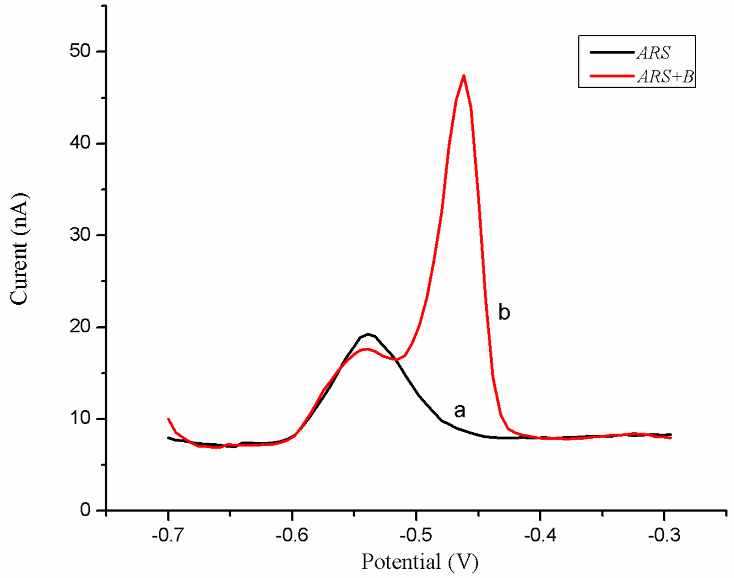


Figure 2. Voltammograms of 1×10^{-5} mol·L^{-1} ARS and 1×10^{-5} mol·L^{-1} ARS + 10 μg·mL^{-1} B in 0.1 mol·L^{-1} ammonium acetate. Other conditions: pulse duration of 0.02 s, pulse amplitude of 50 mV, scan rate at 5 mV·s^{-1}, equilibration time of dropping mercury of 10 s.

3.4. Choice of the determination mode

The VA polarograph has four kinds of working electrode, including the hanging mercury drop electrode (HMDE), the dropping mercury electrode (DME), the static mercury drop electrode (SDME) and the rotating disk electrode (RDE). In our experiment, HMDE and DME were applied. The results indicated signals with HDME have poor reproducibility, whereas signals with DME have good reproducibility and stability. Therefore, DME was chosen as the working electrode.

3.5. Choice of the equilibration time of dropping mercury

In order to prevent oxidation of the mercury drops, the impact of equilibration time of dropping mercury was investigated. Fig. 3 shows the effect of equilibration time of dropping mercury on the peak current. Equilibration time of 2 s, 5 s, 7 s, 10 s, 15 s, 20 s, 25 s and 30 s were studied for the determination of the boron-ARS complex. The results indicated that, the peak current remained stable after 10 s. But the longer equilibration time of dropping mercury, the more consumption of mercury and waste of time. Thus, an equilibration time of 10 s was chosen for the measurement.

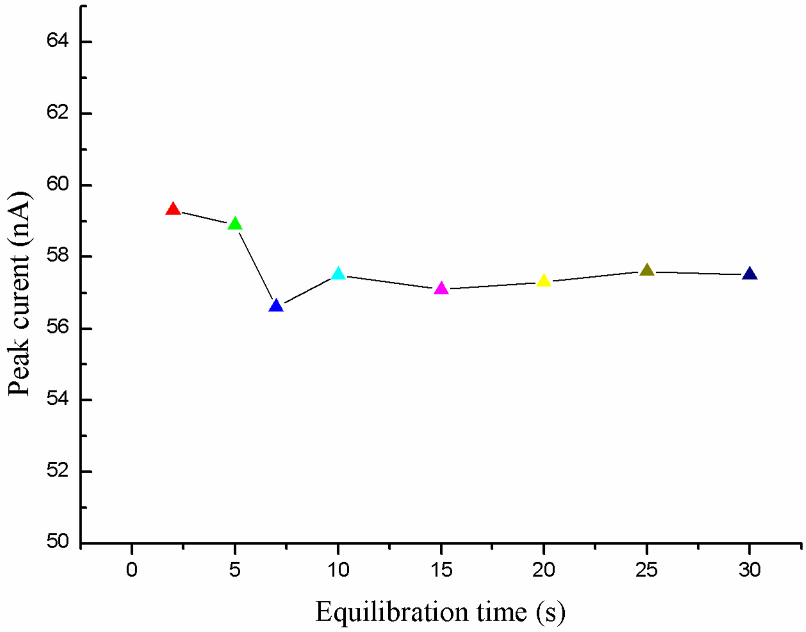


Figure 3. The effect of equilibration time of dropping mercury. Conditions: 1×10^{-5} mol·L^{-1} ARS + 10 μg·mL^{-1} B in 0.1 mol·L^{-1} ammonium acetate, pulse duration of 0.02 s, pulse amplitude of 50 mV, scan rate at 5mV·s^{-1}.

3.6. Choice of the scan rate

Scan rate has a direct impact on the peak potential and peak current, and plays an important role in the electrochemical tests. The scan rate of 4 mV·s^{-1}, 5 mV·s^{-1}, 7 mV·s^{-1}, 10 mV·s^{-1}, 15 mV·s^{-1}

and 20 mV·s^{-1} were examined to determine boron-ARS complex in this experiment. The adsorption of the complex can be clearly observed in differential pulse (DP) scan when the scan rate was 5 mV·s^{-1}, and the peak current is stable and reproducible at this scan rate. At scan rates higher than 5 mV·s^{-1}, the complex peak becomes asymmetric and the peak current is unstable. Therefore, a scan rate of 5 mV·s^{-1} was used in the study.

3.7. Choice of reaction temperature and time of complex reaction

The effect of temperature and time of complex reaction was investigated. The reaction mixture containing 10 μg·mL^{-1} of boron, 1×10^{-5} mol·L^{-1} of ARS at pH 6.5 was heated at 25, 40, 60 and 80 ◦C respectively. After heating to the desired temperature, the resulting solution was allowed to stand for 15 min, 1 h, 4 h and 10 h respectively followed by voltammetric determination. The results indicate that both the reaction temperature and time of complex reaction have little impacts on the peak current, as shown in Fig. 4. For the purpose of convenient and rapid detection, a reaction temperature of 25 ◦C and a reaction time of 15 min were chosen as the complex condition.

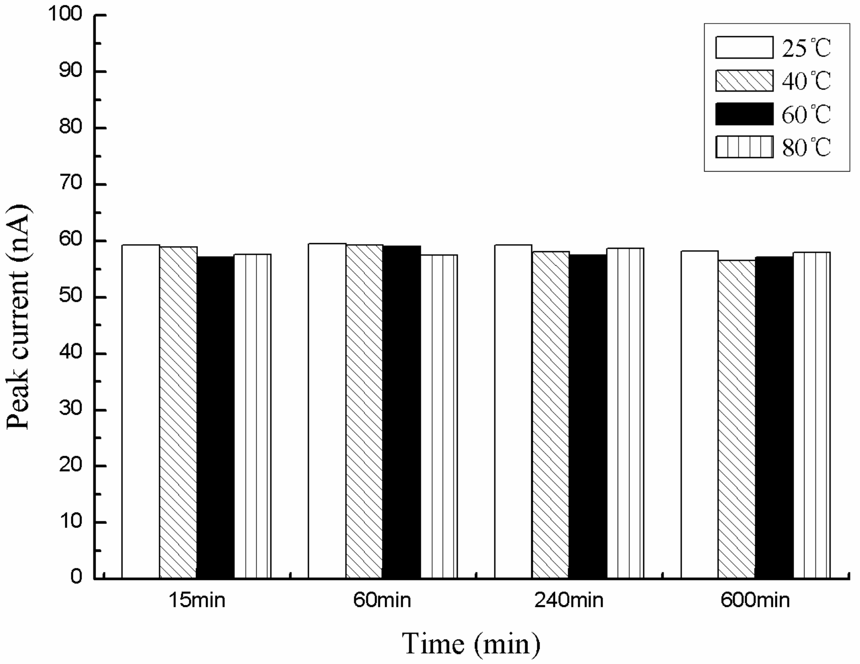


Figure 4. The effect of temperature and time of complex reaction. Conditions: 1×10^{-5} mol·L^{-1} ARS + 10 μg·mL^{-1} B in 0.1 mol·L^{-1} ammonium acetate, pulse duration of 0.02 s, pulse amplitude of 50 mV, scan rate at 5 mV·s^{-1}, equilibration time of dropping mercury of 10 s.

3.8. Choice of ARS concentration

The effect of the ligand concentration on the peak current of the boron-ARS complex was examined by varying the concentration of the ligand in the presence of 10 μg·mL^{-1} boron and supporting electrolyte at pH 6.5. The peak current was studied at a ligand concentration of 1×10^{-3}, 1×10^{-4}, 5×10^{-4}, 1×10^{-5}, 5×10^{-5}, 1×10^{-6}, 5×10^{-6} and 1×10^{-7}mol·L^{-1}, respectively. The results show that the peak height of the boron-ARS complex increases with the increase of ligand concentration. Furthermore, it is found that the peak shape of the complex is asymmetric and the ARS peak overlaps with the boron-ARS complex peak when the concentration of ARS is higher than 1×10^{-5} mol·L^{-1}. So the concentration of ARS was set at 1×10^{-5} mol·L^{-1} in the experiments.

3.9. Choice of the pH and the supporting electrolyte

Fig. 5 shows the effect of solution pH on the peak current. The peak current slightly increased when the solution pH increased from 5.0 to 6.5, but did not increased much after pH=6.5. When solution pH is higher than 6.5, the ARS peak is negligible, and the baseline goes up with the increase of solution pH; when solution pH is lower than 6.5, the ARS peak gradually disappears as the solution pH drops, and at the same time, the peak height of the boron-ARS complex decreases. Based on the results, the optimum pH was identified as 6.5.

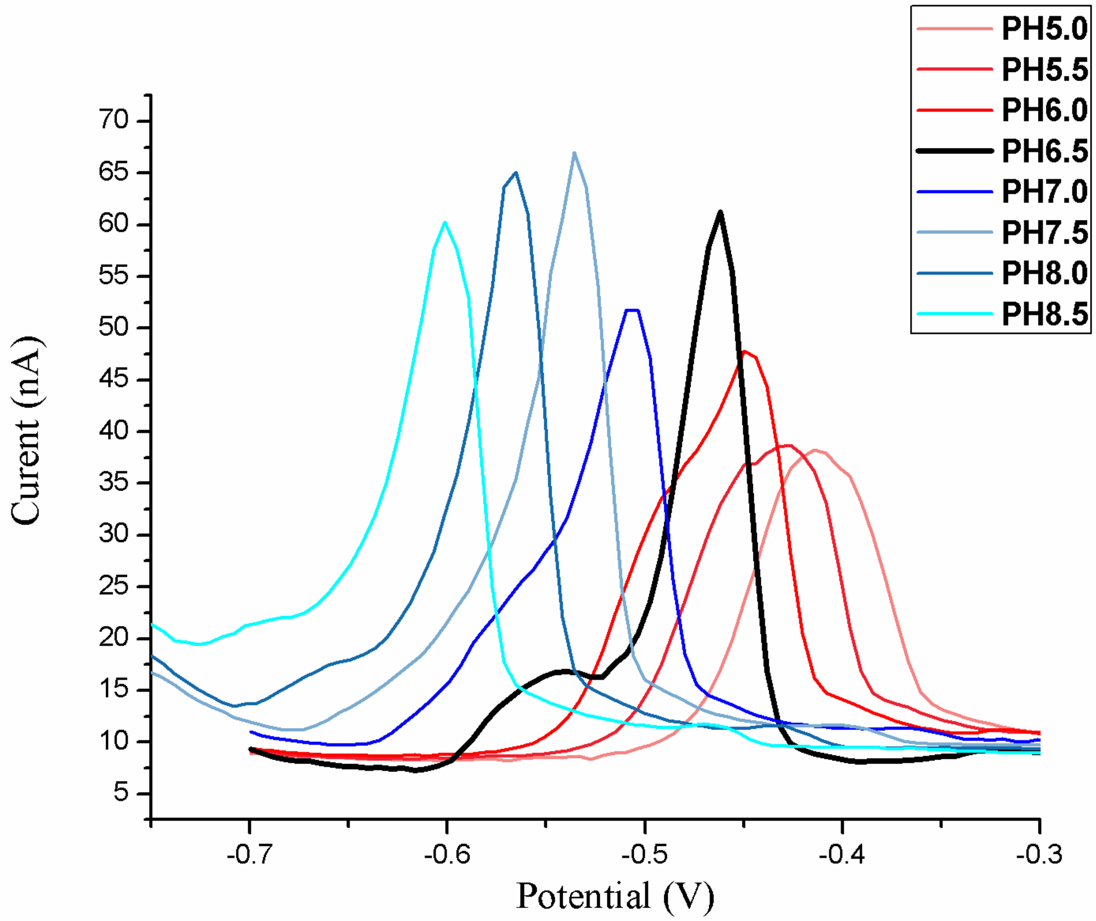
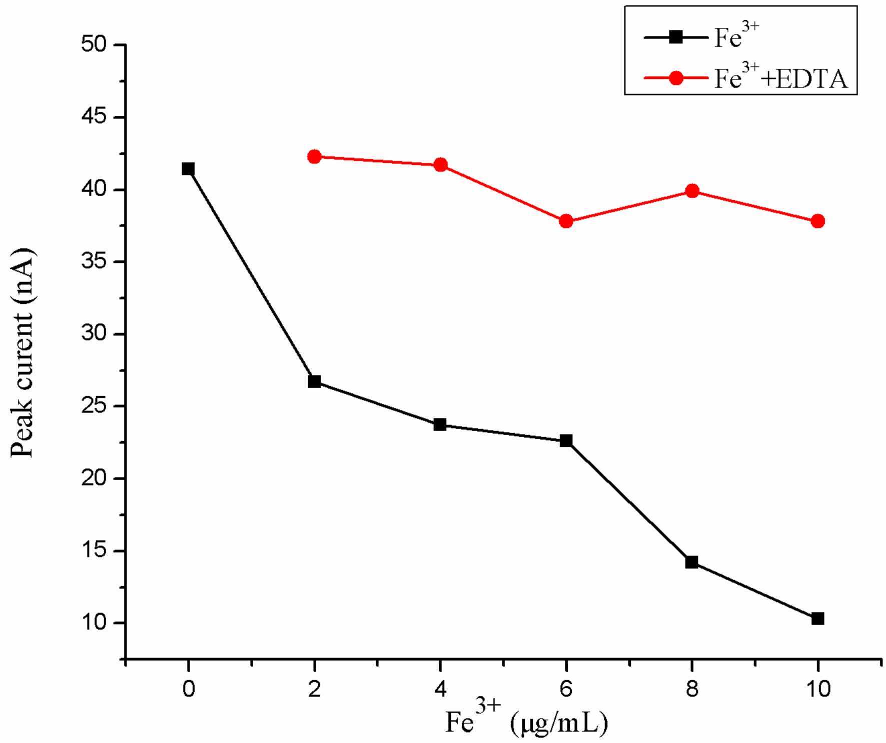


Figure 5. The effect of varing pH. Conditions: 1×10^{-5} mol·L^{-1} ARS + 10 μg·mL^{-1} B in 0.1 mol·L^{-1} ammonium acetate, pulse duration of 0.02 s, pulse amplitude of 50 mV, scan rate at 5 mV·s^{-1}, equilibration time of dropping mercury of 10 s.

A series of electrolytes were studied at pH 6.5 as the supporting electrolyte to identify the optimum supporting electrolyte, electrolytes including ammonium acetate, ammonium acetate-ammonium dihydrogen phosphate, diammonium phosphate, potassium chloride, disodium hydrogen phosphate, sodium dihydrogen phosphate and acetic acid-sodium acetate. The results indicate that ammonium acetate gives the best resolution and it is the most effective in eliminating the migration current.

3.10. Interferences of metal ions, NO^{3-} and F^-

Fe, Al, Ca and some other metal elements are usually present in polysilicon samples, and the presence of these metals could interfere with the stability of peak current of boron-ARS complex. In this part, the interferences of the commonly found metal ions in polysilicon were investigated. The interfering metal ions in various standard concentrations were added to the solution containing 1×10^{-5} mol·L^{-1} of ARS and 10 μg·mL^{-1} of boron to test the impact of these metal ions on the detection. As the results showed in Fig. 6, Fe, Al, Mn and Ti have caused a decrease in peak current while Ca has increased the signal. For the sake of eliminating the interferences of metal ions in peak current, 0.01 mol·L^{-1} EDTA was added to the solution mentioned above. The same experiments were repeated again and the results are showed in Fig. 6. After EDTA added to the solution, the interferences from these metal ions can be eliminated and the peak current can be stabilized at about 40 nA.



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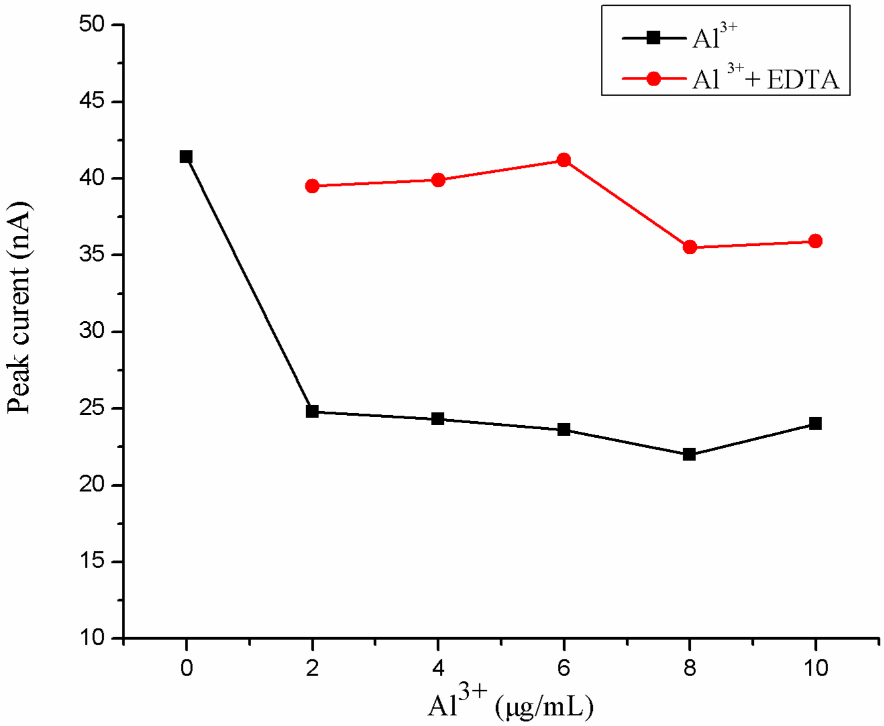
Al3+
Al 3++ EDTA
Peak curent (nA)
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45
40
35
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25
20
15
10
0
2
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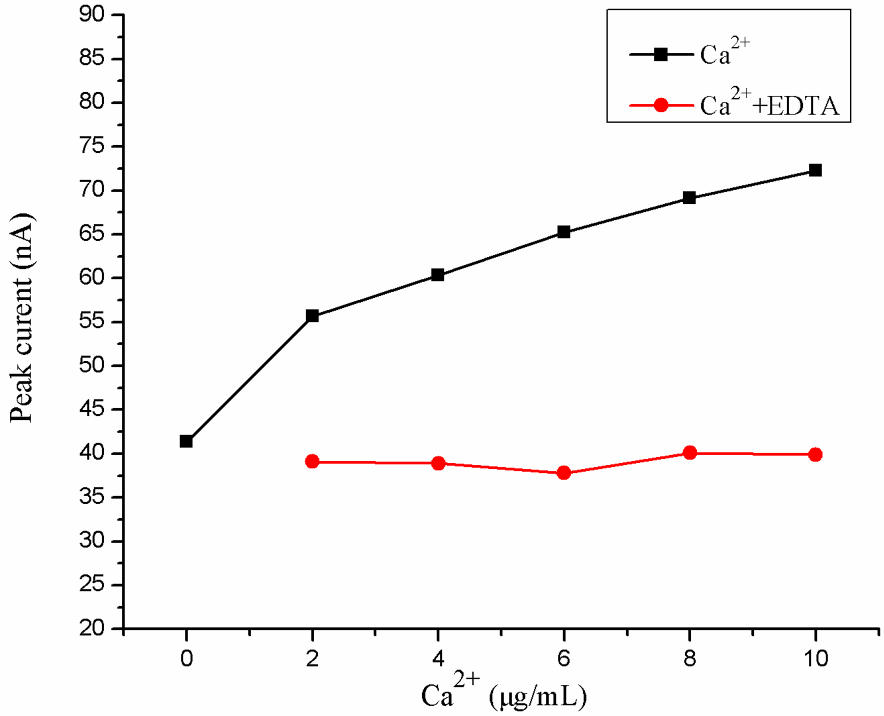
6
8
10
Al3+ (μg/mL)

B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Ca2++EDTA
Peak curent (nA)
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80
75
70
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20
0
2
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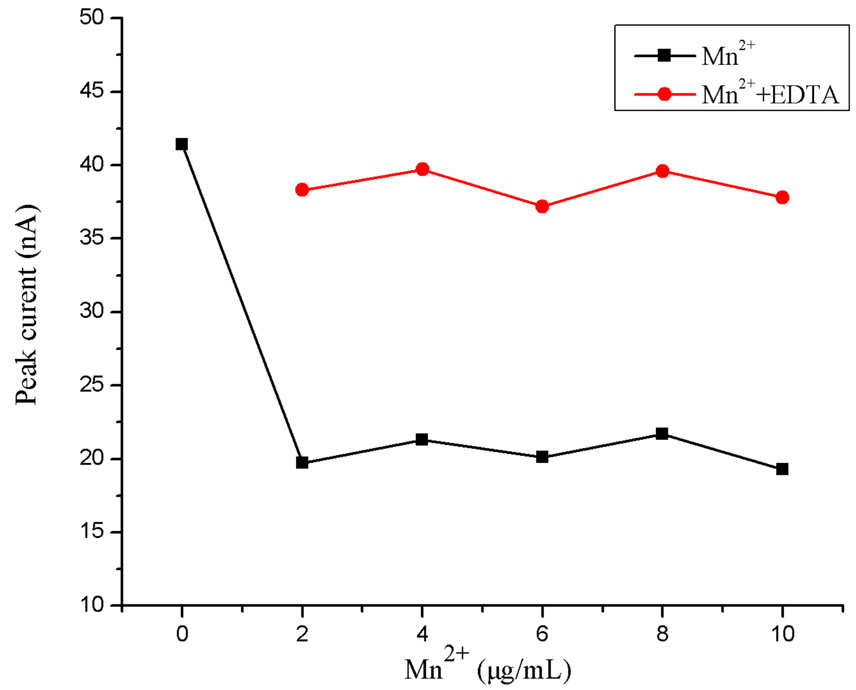
10
Ca2+ (μg/mL)

C



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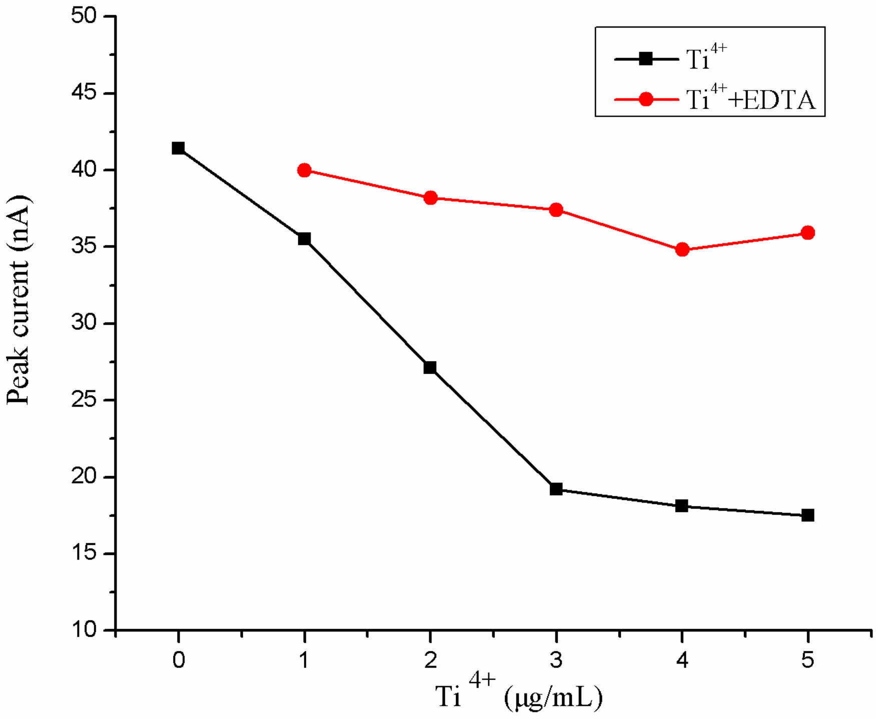
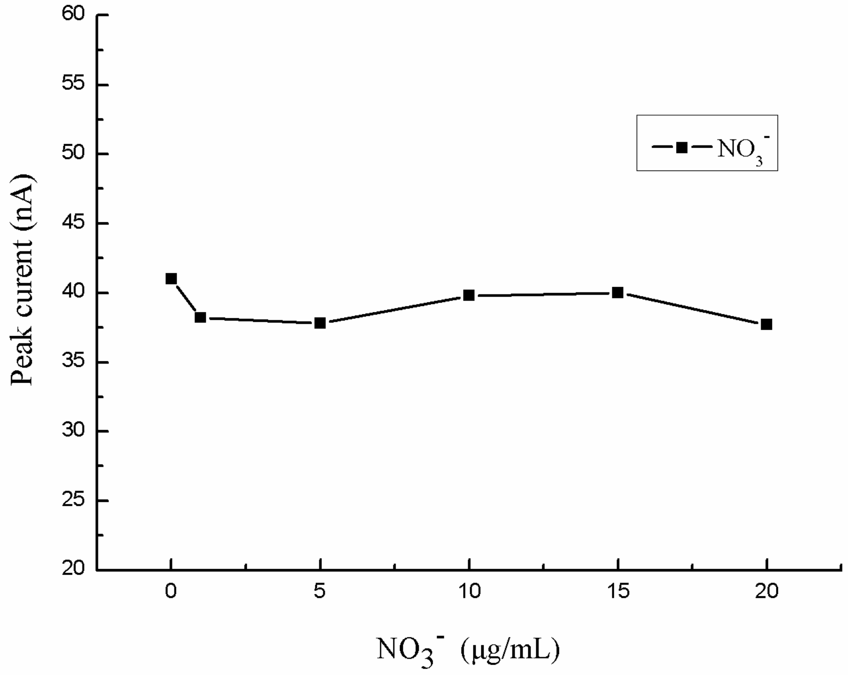


E

Figure 6. The interference and calculation of metal ions. (a) Fe^{3+}, (b) Al^{3+}, (c) Ca^{2+}, (d) Mn^{2+}, (e) Ti^{4+}.

Non-metallic ions NO^{3-} and F^- were introduced as digestion reagents and basically eliminated in the pre-treatment procedure.



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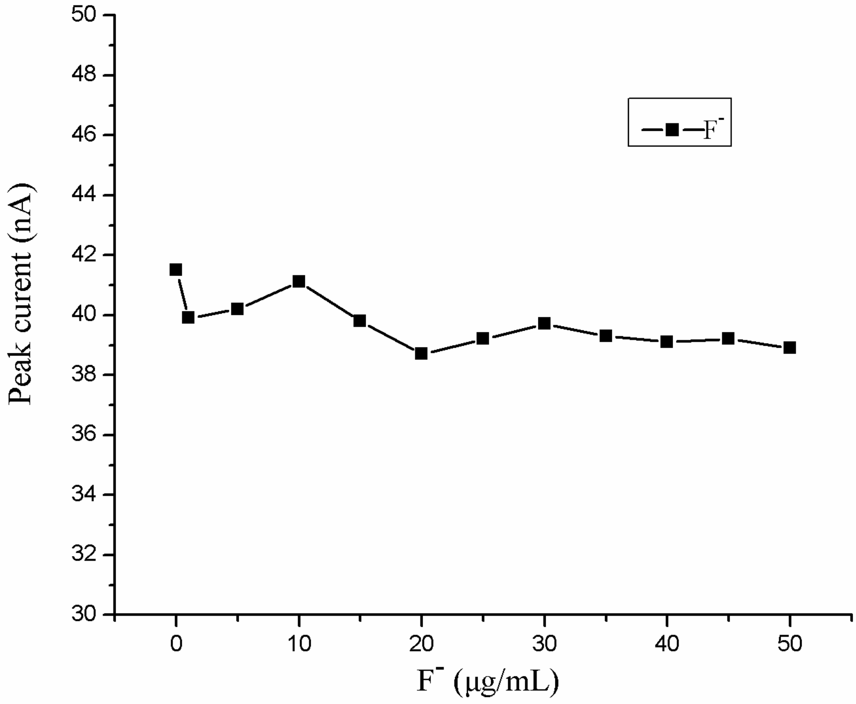


B

Figure 7. The influence of non-metallic ions. (a) NO^{3-}, (b) F^-.

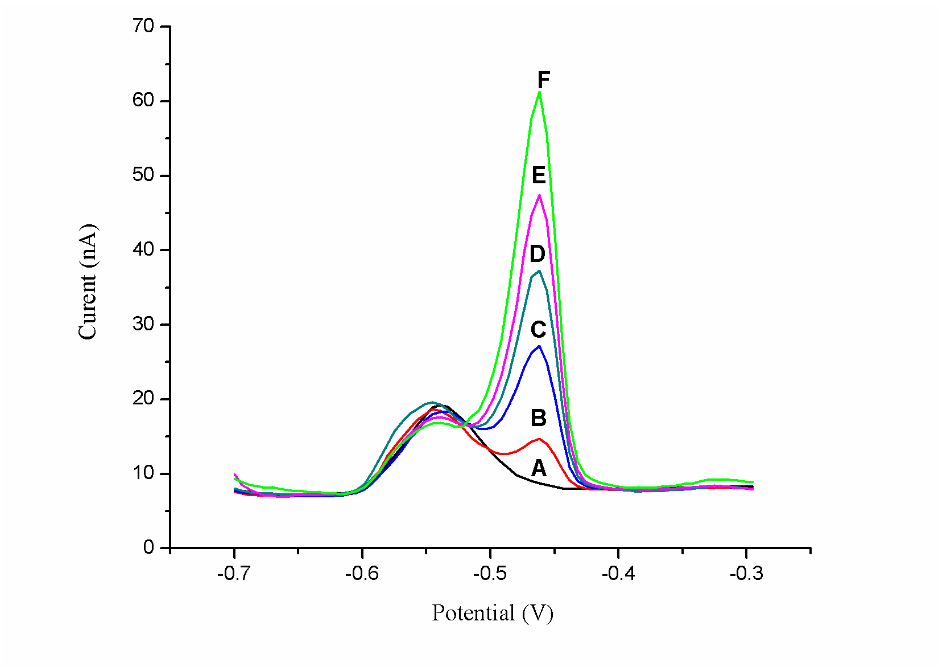
But in order to determine the interference of potential residual NO^{3-} and F^{-}, the following test was conducted. NO^{3-} and F^{-} in various standard concentrations were added to the solution containing 1×10^{-5} mol·L^{-1} of ARS and 10 µg·mL^{-1} of boron, and followed by voltammetric determination. The results show that there is no interference of NO^{3-} and F^{-} on the detection. As shown in Fig. 7, the peak current can be stabilized at about 40 nA in the presence of NO^{3-} and F^{-}. Therefore, even a small amount of residual NO^{3-} and F^{-} exist, there is no significant influence on the detection.

3.11. Standard Curve

Based on the results from the above experiments, the optimum conditions for the determination of boron are summarized in Table 2.

Table 2. Voltammetric parameters for determination

Working electrode	**DME**
Pulse amplitude (mV)	50
Pulse duration (s)	0.02
Scan rate (mV·s^{-1})	5
Equilibration time of dropping mercury (s)	10
Supporting electrolyte, PH	Ammonium acetate buffer, 6.5
Concentration of ARS (mol·L^{-1})	1×10^{-5}



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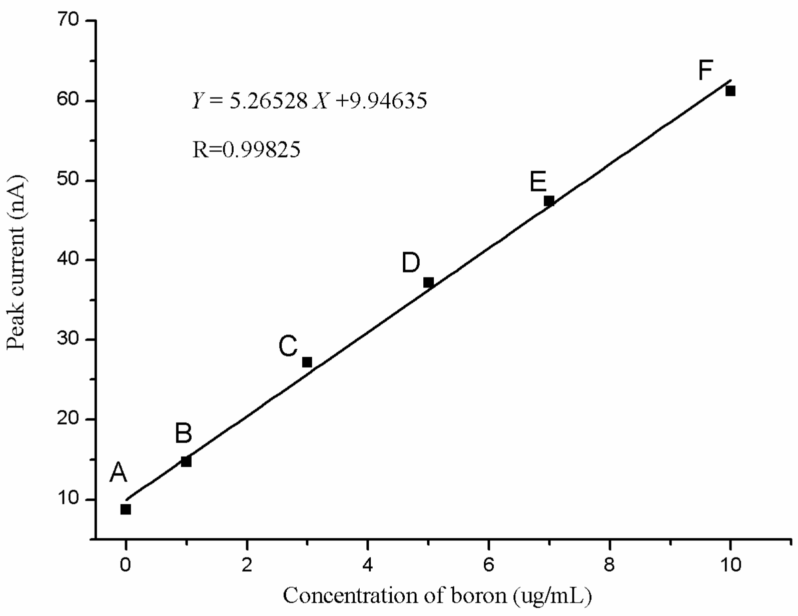

B

Figure 8. (a) Voltammograms obtained for calibration curve, (b) Standard curve. (A) 1×10^{-5} mol·L^{-1} ARS + 0 µg·mL^{-1} boron, (B) 1×10^{-5} mol·L^{-1} ARS + 1 µg·mL^{-1} boron, (C) 1×10^{-5} mol·L^{-1} ARS + 3 µg·mL^{-1} boron, (D) 1×10^{-5} mol·L^{-1} ARS + 5 µg·mL^{-1} boron, (E) 1×10^{-5} mol·L^{-1} ARS + 7 µg·mL^{-1} boron, (F) 1×10^{-5} mol·L^{-1} ARS + 10 µg·mL^{-1} boron.

A calibration curve for boron was established by plotting the peak current of the boron-ARS complex to the concentration of boron under the conditions specified in Table 2. As Fig. 8 shows, the calibration curve is linear in the concentration range of 0-10 µg·mL^{-1} with a regress equation of $Y = 5.26528\ X + 9.94635$ and a correlation coefficient of 0.99825.

3.12. Blank values and detection limit

In order to evaluate the lower detection limit of the present method, it is important to determine the blank values and their standard deviations.

Table 3. Comparison of blank values from the proposed method and ICP-OES method for determination of boron

Sample No	Blank value (µg·mL^{-1}) Proposed method	ICP-OES method	Average of blank values (µg·mL^{-1}) Proposed method	ICP-OES method
1	0.09±0.042	0.13±0.032	0.132	0.098
2	0.13±0.002	0.07±0.028		
3	0.15±0.018	0.09±0.008		
4	0.12±0.012	0.12±0.022		
5	0.17±0.038	0.08±0.010		

Blank tests were run by following the determination procedure listed in *2.3*, without using polysilicon samples. Table 3 shows the results from the blank tests, which were measured five times in parallel. From the results shown in Table 3, the average of blank values is 0.132 μg·mL^{-1}, and the maximum standard deviation is 0.042 μg·mL^{-1}. Therefore, the detection limit, estimated to be three times of the maximum standard deviation (3σ) of the blank values, is 0.12 μg·mL^{-1}.

ICP-OES method was used to compare with the proposed method. Comparative results are listed in Table 3. Obtained by ICP-OES method, the average of blank values is 0.098 μg·mL^{-1}, the maximum standard deviation is 0.032 μg·mL^{-1}, and the detection limit is 0.09 μg·mL^{-1}.

3.13. Determination of boron in polysilicon samples

Table 4. Comparison of the measured values of samples and recoveries of added boron obtained by the proposed method and ICP-OES method

Sample No.	**Current (μg·mL^{-1})**		**Added (μg·mL^{-1})**	**Found (μg·mL^{-1})**		**Recovery (%)**	
	Proposed method	**ICP-OES method**		**Proposed method**	**ICP-OES method**	**Proposed method**	**ICP-OES method**
1	2.18	2.23	1.0	3.08	3.18	90	95.3
2	2.22	2.27	1.3	3.40	3.49	90.8	93.8
3	2.09	2.25	1.5	3.48	3.62	92.7	91.6
4	2.14	2.21	1.7	3.72	3.76	92.9	90.9
5	2.20	2.19	2.0	4.08	4.09	94	94.8

Table 5. Comparison of the precision of the sample obtained by the proposed method and ICP-OES method

		Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
Measured value (μg·mL^{-1})	Proposed method	2.18	2.22	2.09	2.14	2.20
	ICP-OES method	2.23	2.27	2.25	2.21	2.19
Average value (μg·mL^{-1})	Proposed method	2.17				
	ICP-OES method	2.23				
RSD (%)	Proposed method	2.4				
	ICP-OES method	1.4				

The proposed method was applied to the determination of boron in polysilicon samples, and the recoveries of added boron and test precision were determined. Five polysilicon samples (the purity is about 99.99%) were digested and tested according to the testing procedure described in section 2.3. As the results shown in Table 4 and Table 5, the recoveries of the samples are in the range of 90%-94% with a RSD of 2.4%.

Compared with the proposed method, ICP-OES method was used for determining born in the same polysilicon samples. Five polysilicon samples were digested in the same way described in section 2.3 and tested by an ICP-OES instrument of Advantage IRIS from Thermo Electron Corporation (America). As the results shown in Table 4 and Table 5, the recoveries of the samples are in the range of 90.9%-95.3% with a RSD of 1.4%.

4. CONCLUSIONS

In this paper, a new voltammetric method for the determination of trace amounts of boron in polysilicon is developed. First, HNO_3 and HF were used to digest the samples and stabilize the boron during the pretreatment procedure. Thereafter, the concentration of boron was determined by voltammetry with ARS as the complexing agent and ammonium acetate as the electrolyte at pH=6.5. DME used as a working electrode in this method, the mercury drops kept dropping and the electrode surface continuously updated, so the pollution from adsorption of impurity particles in external environment can be reduced.

This method is suitable for determination of trace amounts of boron contained in polysilicon in the range of 1.2 $\mu g \cdot g^{-1}$~100 $\mu g \cdot g^{-1}$ with recoveries in the range of 90%-94% and a RSD of 2.4%. As a consequence, the results obtained from the proposed method and ICP-OES method have no statistically significant difference, but the detection limit of these two methods is higher than 12 $ng \cdot g^{-1}$ of ICP-MS method [22]. To sum up, the proposed method is comparable with ICP-OES and ICP-MS methods in terms of simplicity and costs. Furthermore, the results indicate that the proposed method has good reproducibility and precision.

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References

1. P. K. Chandra, B. J. David, S. Frederick, *Solar Energy Materials and Solar Cells*, 74 (2002) 77.
2. J. J. Wu, W. H. Ma, B. Yang, Y. N. Dai, K. Morita, *Trans. Nonferrous Met. Soc.*, 19 (2009) 463.
3. P. S. Ramanjaneyulu, Y. S. Sayi, V. A. Raman, K. L. Ramakumar, *J. Radioanal Nucl. Chem.*, 274 (2007) 109.
4. S. Thangavel, S. M. Dhavile, K. Dash, S. C. Chaurasia, *Anal. Chem. Acta*, 502 (2004) 265.
5. J. Ciba, A. Chruściel, *Fresenius J. Anal. Chem.*, 342 (1992) 147.
6. Z. J. Li, Z. W. Cui, J. Tang, *Food Chem.*, 94 (2006) 310.
7. P. Carrero, A. Malave, E. Rojas, C. Rondon, Y. P. Pena, J. L. Burguera, M. Burguera, *Talanta*, 68 (2005) 374.

8. Gerwin Zeibig, *Mikrochim. Acta III*, (1989) 389.
9. A.Simsek, S. Korkmaz, Y. S. Velioglu, O. Y. Atman, *Food Chem.*, 83 (2003) 293.
10. A.E. Pillay, J. R. Williams, M. O. Eimardi, S. M. Hassan, A. A. Hamdi, *J. Radioanal Nucl. Chem.*, 254 (2002) 315.
11. S. Kozono, M. Yagi, R. Takashi, *Anal. Chem. Acta*, 368 (1998) 275.
12. M. Mihaljevic, O. Sebek, E. Lkesova, A. Bouzkova, *Fresenius J. Anal. Chem.*, 371 (2001) 1158.
13. M. Burguera, J. L. Burguera, C. Rondon, P. Carrero, *Spectrochimica Acta Part B*, 56 (2001) 1845.
14. A.D. Carbo, S. S. Ramos, D. J. Y. Marco, M. M. Moreno, J. V. G. Adelantado, F. B. Rerig, *Anal. Chem. Acta*, 501 (2004) 103.
15. P. S. Ramanjaneyulu, Y. S. Say, T. N. Nathanniel, A. V. R. Reddy, K. L. Ramakumar, *J. Radioanal Nucl. Chem.*, 273 (2007) 411.
16. S. S. Ramos, F. B. Reig, J. V. G. Adelantado, D. J. Y. Marco, A. D. Carbo, J. A. B. Perez, *Spectrochimica Acta Part B*, 55 (2000) 1669.
17. Radhika M. Rao, Suresh K. Aggarwal, *Talanta*, 75 (2008) 585.
18. S. Wei, J. Kui, *Talanta*, 56 (2002) 1073.
19. N. Chimpalee, D. Chimpalee, B. Boonyanitchayakul, D. Thorburn Burns, *Anal. Chem. Acta* 282 (1993) 643.
20. Ibrahim Sahin, Nuri Nakiboglu, *Anal. Chem. Acta*, 572 (2006) 253.
21. http://sti.srs.gov/fulltext/ms9800595/ms9800595.html (last accessed 05/26/2010).
22. Irina E. Vasilyeva, Elena V. Shabanova, Yulya V. Sokolnikova, Olga A. Proydakova, Valery I. Lozhkin, *Journal of Analytical Atomic Spectrometry*, 14 (1999) 1519.