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SPECTROPHOTOMETRIC DETERMINATION OF BORON IN THE SUBMICROGRAM RANGE*

M. P. Menon

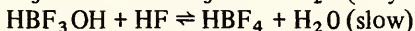
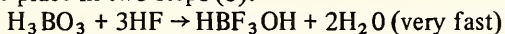
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INTRODUCTION

The use of boron as dopant in silicon semiconductors has generated considerable interest in the analytical methods for the quantitative determination of boron in the submicrogram range. Vick and Whittle (1) have shown that the surface concentration of boron in silicon wafers increases with temperature and reaches a plateau of about 2.5×10^{20} atoms/cm³ at 1200°C. The shape of the concentration profile depends on the temperature and other conditions of doping technique. Although the differential sheet conductance technique has been used for profiling boron in silicon wafers, it has been suggested (2) that these profiles may be different from the actual distribution due to the presence of electrically inactive boron in the form of precipitates. A chemical profiling technique would, therefore, be required for the determination of the total boron profile.

Of the various chemical analytical techniques reported in the literature the spectrophotometric method developed by Ducret (3) appears most attractive in regard to speed and sensitivity. This method has been improved by Pasztor and Bode (4) and also by Utsumi and others (5). The sensitivity for this method as reported by the former is 0.2/μg while the latter claims a detection limit of $0.05 \pm 0.02/\mu\text{g}$. To run a satisfactory profile down to 10^{18} atoms/cm³ of boron in silicon wafers a sensitivity of about 10^{-9} g of B is required.

The spectrophotometric method is based on the conversion of boron into tetrafluoroboric acid and the extraction of the BF₄-methylene blue complex into 1,2-dichloroethane. By measuring the absorbance of the colored complex in the organic solvent at 6600 Å, traces of boron can be determined. The reaction between boric acid and hydrofluoric acid is known to take place in two steps (6):



The time required to reach equilibrium is approximately 218 minutes at a boron concentration of 0.11 M/l, but it increases with decreasing boron concentration. Ducret (1) and others (4) have accelerated the reaction by taking a very large excess of HF while Utsumi et al (5) reduced the time further to thirty minutes by adding dilute H₂SO₄. The sensitivity of the above method will undoubtedly depend, among others, on (1) the amount of the colored complex extracted into

* This work was performed by the author at IBM Thomas Watson Research center, Yorktown Heights, N.Y., as a summer faculty employee. (1969).

the organic layer, (2) the absorbance of the blank and (3) the path length of the cell used for absorbance measurements. It was found that the conditions chosen for the analysis in the previous work could be modified to increase the sensitivity.

In this work attempts were made to enhance the sensitivity of the spectrophotometric method by changing the various parameters involved in the analysis. Although various procedures were tried only the most promising one is reported here. A new radioreagent method which was also investigated for the analysis of boron has been reported elsewhere(7).

EXPERIMENTAL

Reagents:

Boric acid, 1,2-dichloroethane (certified-Fisher Scientific Co.), HF(Ultra pure, 40%) (E. Merk AG Darmstadt, Germany), methylene blue bromide (Alfa Inorganic, Ventron) were used in this work. Boric acid solution was standardized potentiometrically using mannitol and its molarity was found to be $9.28 \times 10^{-3} \text{M/l}$. From this stock solution, working solutions containing 10^{-6}g/ml , 10^{-7}g/ml and 10^{-8}g/ml were prepared by dilution.

Equipment used:

Cary Model 14 Recording Spectrophotometer.

Procedure:

One milliliter of the solution containing various amounts of boron, in the form of boric acid, is treated with one milliliter of 0.5M/l HF and allowed to stand for 8 hours or more. The mixture is then diluted to 9 ml with water and mixed with 1 ml of 10^{-3}M/l methylene blue solution. This is shaken with 20 ml of 1,2-dichloroethane for one minute. After the separation of the two layers, about 18 ml of the organic layer is transferred to another separatory funnel and washed with 5 ml of water. The extract is dried with a small amount of anhydrous Na_2SO_4 and the absorbance measurements are made in a 5cm cuvette. The time dependance of the formation of HBF_4 under these conditions was determined by measuring the absorbance of a 0.5 μg boron solution as a function of time. The curve given in Fig. 1 shows that it takes at least 8 hours for the reactants to come to equilibrium under the above conditions.

The net absorbance may be further increased by extracting with 30 ml of 1,2-dichloroethane, washing the extract with 10 ml of water and measuring the absorbance in a 10 cm cell.

RESULTS AND DISCUSSIONS

The results of the analysis of boron standards using 20 ml of the extractant and 5 cm path length are presented in Table I. The net absorbance is based on the average of the blanks determined on the same day of the analysis. It is interesting to note that a higher absorbance and better reproducibility than in the previous work was obtained in the entire concentration range. The higher absorbance obtained in this procedure, when compared to that in reference (5), is believed to result from a higher extraction of BF_4 -methylene blue complex under the proposed conditions.

Ducret (3) has reported that 80-85% of BF_4 -methylene blue complex is extracted into 1,2-dichloroethane if the phase volumes are in the ratio 1:1. The extraction efficiency E, in percent of the complex extracted, is given by the relation:

$$E = \frac{100.D}{D + v_{\text{aq}}/v_{\text{org}}}$$

where D is the distribution coefficient and is equal to four in this system, V_{aq} and V_{org} are the volumes of the aqueous phase and organic phase, respectively. E will therefore, increase with decreasing $V_{\text{aq}}/V_{\text{org}}$ ratio. The volume ratio used in previous work was above one while in the present work it is 0.5.

The concentration of boron in an unknown sample can be measured by analysing the sample in the same manner and using a calibration curve based on the measurements of boron standards. Following the above procedure, 3×10^{-8} g of boron can be determined with a relative standard deviation of 30%, provided samples and standards are processed on the same day.

ACKNOWLEDGEMENT

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REFERENCES

1. Vick, G. L. and Whittle, K.M., J. Electrochem. Soc.: Solid State Science, 116, 1142 (1969).
2. Makris, IBM Report (Private Communication).
3. Ducret, L., Anal. Chim. Acta., 17, 213 (1957).
4. Pasztor, L. and Bode, J. D., Anal. Chem., 32, 277 (1960).
5. Utsumi, S. Ito, S. and Isozaki, A., J. Chem. Soc. Japan, 86, 921 (1965).
6. Wamser, C.A., J. Am. Chem. Soc., 70, 1209 (1948).
7. Menon, M. P., Paper submitted to Radioanalytical Chemistry.

TABLE I

Results of the Absorbance Measurements for the Analysis of Boron

Conc. of B (gram)	Gross Absorbance	Blank Used	Net Absorbance
5×10^{-7}	1.429	$0.177 \pm .017$	$1.270 \pm .025$
	1.465	$0.177 \pm .017$	
3×10^{-7}	0.996	$0.177 \pm .017$	$0.799 \pm .027$
	0.955	$0.177 \pm .017$	
2×10^{-7}	0.665	$0.177 \pm .017$	$0.500 \pm .021$
	0.690	$0.177 \pm .017$	
1×10^{-7}	0.399	$0.152 \pm .018$	$0.246 \pm .018$
	0.401	$0.152 \pm .018$	
	0.395	$0.152 \pm .018$	
	0.421	$0.175 \pm .015$	
8×10^{-8}	0.345	$0.152 \pm .018$	$0.182 \pm .025$
	0.312	$0.152 \pm .018$	
	0.350	$0.175 \pm .015$	
5×10^{-8}	0.252	$0.152 \pm .018$	$0.097 \pm .020$
	0.260	$0.152 \pm .018$	
	0.248	$0.152 \pm .018$	
	0.260	$0.175 \pm .015$	
3×10^{-8}	0.183	$0.152 \pm .018$	$0.036 \pm .020$
	0.199	$0.152 \pm .018$	
	0.190	$0.152 \pm .018$	
	0.202	$0.175 \pm .015$	

Effect of Washing on the Absorbance of the Blank

<u>Blanks</u>	<u>Wash Steps</u>	<u>Absorbance</u>
1	no wash	1.055
	1st wash	0.245
	2nd wash	0.130
2	no wash	1.015
	1st wash	0.230
	2nd wash	0.108

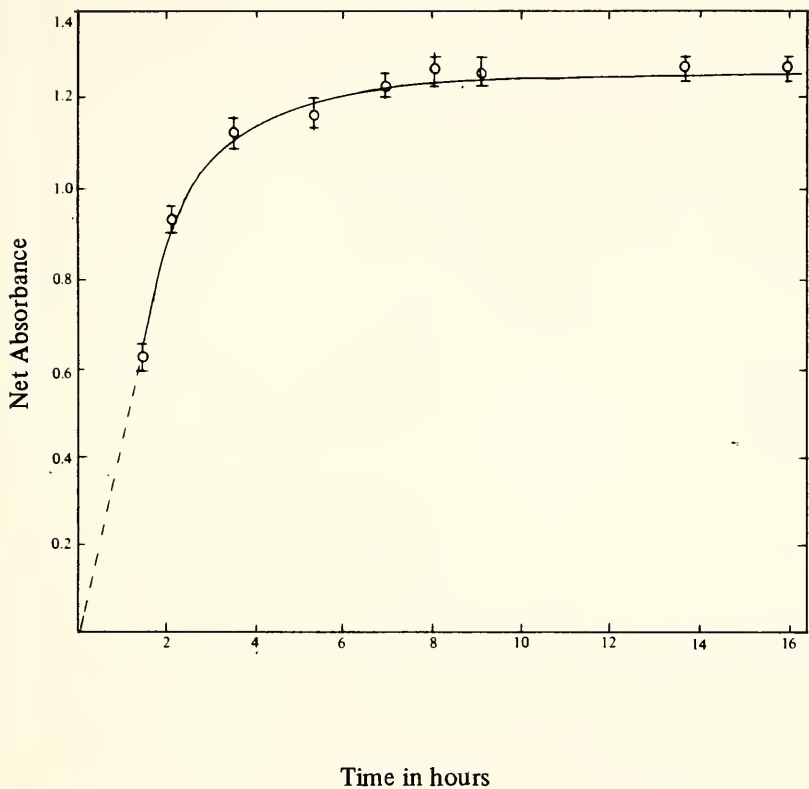


Fig. 1 Time dependence of the formation of HBF_4 using the spectrophotometric method. (Each Reaction Mixture: $4.65 \times 10^{-5} \text{M}$ H_3BO_3 + 0.25M HF).