

Short communication

## Measurement of trace phosphorus in dichlorosilane by high-temperature hydrogen reduction gas chromatography

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### Abstract

Dichlorosilane, a gas at normal temperature with a boiling point of 8.3°C, is very difficult to sample and detect using conventional methods. We reduced phosphorus in dichlorosilane to PH<sub>3</sub> by hydrogen at high temperature, then PH<sub>3</sub> was separated from chlorosilanes by NaOH solution and from other hydrides by chromatographic absorption. Thus the problem of interference of chlorosilanes and other hydrides was overcome and PH<sub>3</sub> was measured by a double flame photometric detector at 526 nm. This method was sensitive, reliable and convenient and the sensitivity reached as low as 0.04 µg/l.

**Keywords:** Hydrogen reduction; Dichlorosilane; Phosphorus

### 1. Introduction

High purity dichlorosilane, SiH<sub>2</sub>Cl<sub>2</sub>, (DCS) is a new silicon gaseous source used in the electronic industry. DCS is mainly used in silicon epitaxy and preparation of silicon nitride or polycrystalline silicon for large-scale integrated circuits. The silicon epitaxy temperature can be reduced by about 100°C when SiH<sub>2</sub>Cl<sub>2</sub> is used as source reactant instead of SiCl<sub>4</sub>. This can help to depress thermal defects, reduce the transition width and improve the quality of the epilayers. At normal temperature DCS is easy to liquefy with constant pressure. So its flux is easily controlled during semiconductor process. The phosphorus content of DCS, which directly affects the purity of the epilayers, is a key index and has been extensively investigated. Spectrophotometry [1] was

used to measure the phosphorus content in DCS in 1970s. However, chemical enrichment and large sample volume were unavoidable, which made the process complicated. In the 1980's, ion-chromatography [2] was used to measure trace phosphorus. This method demands that the sample must be in an ionized state. Although gas chromatography [3,4] was also used in this period, the main gas was separated by using two long chromatographic columns. Schulte et al. [5] isolated PCl<sub>3</sub> and POCl<sub>3</sub> from SiHCl<sub>3</sub> by using gas chromatography and reported a lower phosphorus detection limit of 0.1 µg/l. Ezheleva et al. [6] analysed phosphorus in silane by using a flame photometric detector. Silane was segregated by a alkaline column filled with KOH and Al<sub>2</sub>O<sub>3</sub>. The sensitivity was reported to be 3.5 µg/l. In late 1980s, we used high-temperature hydrogen reduction of phosphorus instead of two very long chromatographic columns. However, it

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could only be used to determine phosphorus content in trichlorosilane (TCS). DCS is a very reactive liquid with a boiling point of 8.3°C, so its sampling is very difficult.

In this paper DCS sampling at low temperature (−78°C) is adopted by us. Based on thermodynamic calculation [7,8] and experimental data, we have found the optimum reduction temperature of phosphorus in DCS and reduced it to  $\text{PH}_3$ . A method for separating  $\text{PH}_3$  from chlorosilanes by NaOH solution is proposed and the problem of interference of chlorosilanes is overcome. After separation from other hydrides by using chromatographic absorption,  $\text{PH}_3$  is measured by a double flame photometric detector at 526 nm. The sensitivity reaches as low as 0.04  $\mu\text{g/l}$ .

## 2. Principle

First, the liquefied DCS is injected into a high-temperature furnace tube filled with quartz fragments. DCS is partly decomposed in hydrogen atmosphere at 760°C, the phosphorus impurity in form of phosphorus chloride or in other forms is reduced by hydrogen to  $\text{PH}_3$  [9,10]. Then  $\text{PH}_3$  is separated from unreacted DCS and other by-product chlorosilanes by two-stage NaOH solution separation

and enters into chromatographic column, where  $\text{PH}_3$  is segregated from other hydrides. The  $\text{PH}_3$  signal is detected by a double flame photometric detector at 526 nm, recorded and amplified. By comparing with the standard peak height, the phosphorus content in DCS can be obtained. When reduction temperature is 760°C, the minimum detectable phosphorus quantities of this method reaches 0.006 ng and the sensitivity is 0.04  $\mu\text{g/l}$  for the sampling quantity of 0.1 ml.

## 3. Experiment

### 3.1. Apparatus

The apparatus consists of three parts: high temperature reduction furnace, separating and detecting system (Fig. 1).

### 3.2. Reagents

High purity DCS, TCS and  $\text{PCl}_3$ .

### 3.3. Experimental parameters

The experimental parameters are shown in Table 1.

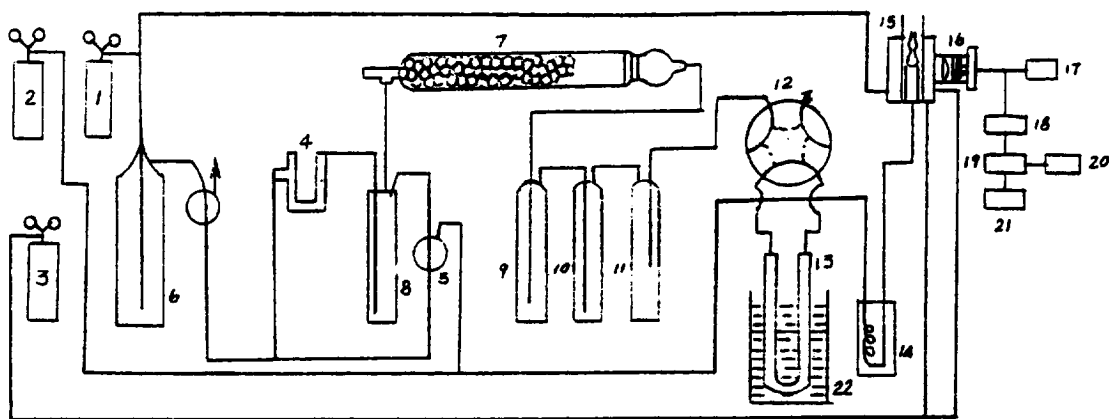


Fig. 1. Schematic diagram of analytical system. 1 =  $\text{H}_2$ ; 2 =  $\text{N}_2$ ; 3 = air; 4 = sample entrance; 5 = three-way valve; 6 = purifier; 7 = reduction furnace tube filled with quartz fragments; 8 = four grade counter current mixer; 9, 10 = separator with NaOH; 11 = dehydrator; 12 = six-way valve; 13 = collector filled with quartz pills coated with silicon oil type DO550 (a substance with chemical composition of methyl phenyl polysiloxanol); 14 = separator filled with 60 mesh porous pills consisting of polymer of divinylbenzene type GDX101; 15 = double flame photometric detector; 16 = electronic system of detector; 17 = high voltage source; 18 = amplifier; 19 = microprocessor; 20 = electronic potentiometer; 21 = printer; 22 = liquid nitrogen (−78°C) or hot water bath (90–100°C).

Table 1  
Experimental parameters

<i>Reduction system</i>	
Reducing H <sub>2</sub> flow (ml/min)	158
Carrying H <sub>2</sub> flow (ml/min)	40
Mixing chamber temperature (°C)	150
Reduction temperature (°C)	760
Sampling volume (ml)	0.1
<i>Gas chromatography system</i>	
Carrying Ar (ml/min)	57
Flame H <sub>2</sub> (ml/min)	238
Air 1 (ml/min)	92
Air 2 (ml/min)	182
Detector temperature (°C)	100
Voltage (v)	700
Chromatographic temperature (°C)	100

### 3.4. Standard solution and the working curve

We used liquefied low temperature DCS to prepare standard solution for measurement. In our experiments two sets of standard  $\text{PCl}_3$  solution were prepared. One used a mixture of DCS liquefied under  $-10^\circ\text{C}$  and TCS as diluent. The ratio of DCS/TCS is 1/9. Another set of standards was prepared by using pure TCS as diluent. Adding different amounts of these two diluents, two sets of standard  $\text{PCl}_3$  solutions were obtained. The concentrations of  $\text{PCl}_3$  in each standard solution were 0.12, 0.28, 0.56, 1.12 and 2.24 ng/ml, respectively. The sampling volume of each measurement was set to be 0.1 ml. Plotting the dependence of peak height with concentration of phosphorus, the working curves were obtained (Fig. 2). It can be seen from Fig. 2 that the two working curves using mixture of DCS and TCS as diluent, respectively, coincided with each other well.

### 3.5. Experimental procedure

An 0.1-ml sample of DCS liquefied at  $-78^\circ\text{C}$ , the weight of which was 0.15 mg was injected through the sample entrance (4 in Fig. 1) into the analytical system. At room temperature DCS was vaporized then mixed and carried by H<sub>2</sub> into reduction furnace (7 in Fig. 1), in which DCS decomposed or changed into other chlorosilanes and the phosphorus impurity reduced to  $\text{PH}_3$ . Then, unreacted DCS and other chlorosilanes were hydrolyzed by NaOH solution (9–11 in Fig. 1), whereas  $\text{PH}_3$  and H<sub>2</sub> went through

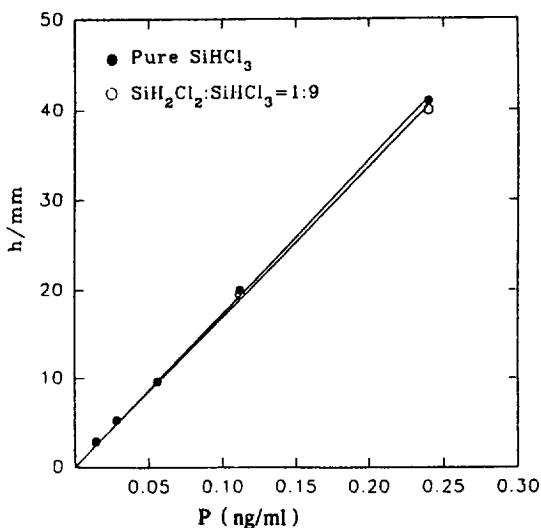


Fig. 2. Working curves.

a six-way valve (12 in Fig. 1) into a collector filled with quartz pills coated with silicon oil type DC550 (13 in Fig. 1).  $\text{PH}_3$  was condensed in the collector at temperature of liquid nitrogen, meantime hydrogen went to vent. During this step the position of the six-way valve is shown in Fig. 3a. After completion of  $\text{PH}_3$  collection (about 15 min) the position of the six-way valve was rotated by  $60^\circ$ , as shown in Fig. 3b. Then nitrogen flowed into the collector, the temperature of which was increased to  $\sim 90^\circ\text{C}$ – $100^\circ\text{C}$  and the mixture of  $\text{N}_2$  and  $\text{PH}_3$  entered into a separator (14 in Fig. 1). The separator was filled with 60 mesh porous pills, consisting of polymer of divinylbenzene type 6DX-101. After separating from other hydrides,  $\text{PH}_3$  flowed into a double flame photometric detector system (15–20 in Fig. 1), where  $\text{PH}_3$  was detected, amplified and recorded. The concentration of phosphorus in DCS was determined by using the working curve.

## 4. Results and discussion

(1) In order to find the optimum reduction temperature of phosphorus we studied the dependence of intensity of  $\text{PH}_3$  peak with reduction temperature (Fig. 4). Based on thermodynamic calculation and

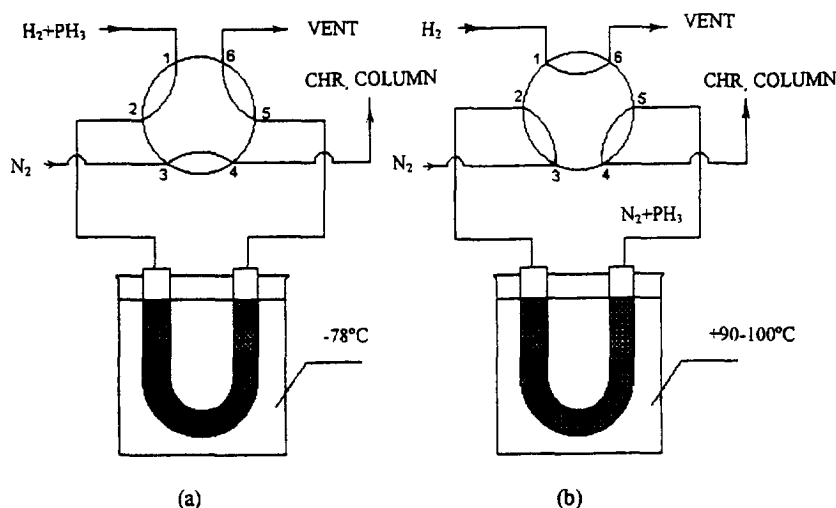


Fig. 3. The working condition of six-way valve (a) during collection of  $\text{PH}_3$ , (b) during release of  $\text{PH}_3$ .

Fig. 4 it was found that the optimum reduction temperature was  $760^\circ$ .

(2) We measured a high-purity DCS sample repeatedly ( $n=9$ ) and found that the average phosphorus concentration was  $0.056 \mu\text{g/l}$ . The standard deviation ( $\sigma$ ) and relative standard deviation ( $S$ ) were 0.0053 and 0.095, respectively, which means good repeatability of our method.

(3) We have analysed crude DCS containing much more phosphorus impurity by using this method and colorimetry and the results are shown in Table 2. These two methods agree with each other very well.

(4) While analysing phosphorus in  $\text{SiHCl}_3$ ,  $\text{SiH}_2\text{Cl}_2$  or  $\text{SiCl}_4$ , it was very difficult to separate trace quantities of  $\text{PH}_3$  from massive amounts of chlorosilanes, which were a big problem in the analysis of phosphorus. We have successfully solved this problem by using NaOH solution separation. After NaOH separation all kinds of chlorosilanes turn into soluble  $\text{Na}_2\text{SiO}_3$ , at the same time  $\text{PH}_3$  does not react. Due to the complete separation chlorosilanes do not enter the flame photometric detector and hydrolysis with formation of white film on surface of quartz window no longer takes place.

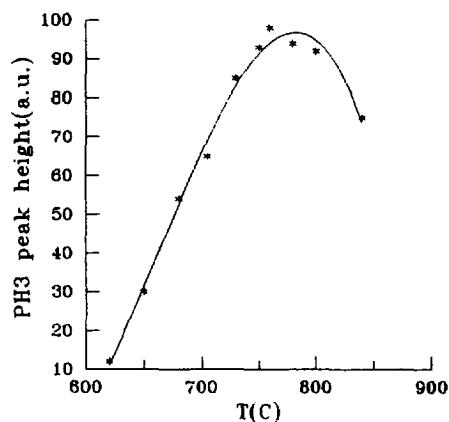


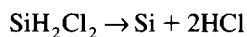
Fig. 4. The dependence of intensity of  $\text{PH}_3$  peak on reduction temperature.

Table 2  
Comparison of different analytical methods for crude DCS

Crude DCS	Determined phosphorus content (%)	
	This method	Colorimetry
1	$8.5 \times 10^{-7}$	$6.0 \times 10^{-7}$
2	$9.0 \times 10^{-7}$	$9.9 \times 10^{-7}$
3	$9.5 \times 10^{-7}$	$6.0 \times 10^{-7}$
4	$1.3 \times 10^{-6}$	$1.2 \times 10^{-6}$
5	$6.7 \times 10^{-6}$	$8.7 \times 10^{-6}$
6	$5.6 \times 10^{-6}$	$7.3 \times 10^{-6}$
7	$4.5 \times 10^{-5}$	$4.8 \times 10^{-5}$
8	$1.9 \times 10^{-5}$	$1.3 \times 10^{-5}$
9	$1.9 \times 10^{-5}$	$1.1 \times 10^{-5}$
10	$7.2 \times 10^{-8}$	$<3.6 \times 10^{-7}$
11	$4.7 \times 10^{-8}$	$<3.6 \times 10^{-7}$
12	$8.8 \times 10^{-8}$	$<3.6 \times 10^{-7}$

Thus the problem of interference of chlorosilanes is overcome.

(5) Several DCS samples were analysed by using this method and the phosphorus concentration was found to be 0.06  $\mu\text{g/l}$ . Then, silicon epilayers were grown using these DCS as silicon source by the Institute of Semiconductors. The reaction is:



The electrical resistivity of the epilayer is about 150  $\Omega\text{-cm}$  and the phosphorus content calculated from resistivity agrees with analytical data.

## 5. Conclusion

An analytical method for measurement of trace quantities of phosphorus in dichlorosilane by high temperature reduction gas chromatography has been proposed. The method is sensitive, reliable and safe and the sensitivity reaches as low as 0.04  $\mu\text{g/l}$ .

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