

New method for determination of arsenic content in tail gases during semiconductor processing

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Abstract—A new method for determination of arsenic content in tail gases during semiconductor processing was proposed. Arsenic compounds of various forms including gaseous, liquid and solid form are reduced by hydrogen at high temperature and analyzed by gas chromatography. Two sampling methods, i. e. sampling by low temperature concentration and sampling by solution absorption were introduced. The analytical method is rapid, sensitive and reliable comparing with other methods.

Keywords: arsenic; tail gases; semiconductor processing.

1 Introduction

With the development of high technology, a plenty of toxic chemicals such as arsine, phosphine, silane, gallium arsenide, indium phosphide, arsenic, phosphorus, arsenic oxides and phosphorus oxides are used during semiconductor materials and devices fabrication (Wen, 1991; Richard, 1988; Xie, 1970). These toxic materials may be emitted into atmosphere along vent tubes with tail gases, causing serious environment pollution. Therefore tail gases should be analyzed before and after abatement processes. For this purpose a new method for analyzing gaseous, liquid and solid arsenide was proposed. In this method arsenide of various forms are reduced by hydrogen at high temperature into AsH_3 and then the concentration of AsH_3 is analyzed by gas chromatography. The method is capable to determine gaseous, liquid and solid samples and can be used for analyzing samples taken from atmosphere, tail gases, waste water, semiconductor and metal materials.

2 Instruments and chemicals

For determination of arsenic content, the necessary instruments and chemicals are as follows: gas chromatograph SP-3700; hydrogen reduction system; automatic recorder; atmospheric sampler; low temperature concentrator-sampler; solution-absorption sampler; high molecular pill (60-80 mesh); micro glass injector; gas chromatographic silica gel (60-80 mesh); NaOH (GR); H_2O_2 (MOS grade); absolute ethyl alcohol (AR); liquid nitrogen; high purity hydrogen; compressed air; standard arsine; standard arsenic solution.

3 Principle of analysis and operating condition

First, gaseous, liquid or solid samples of arsenide are reduced into hydrides at high tempera-

ture by hydrogen and then carried by hydrogen into low temperature concentrator - sampler in which AsH_3 is condensed. After desorption, AsH_3 flows through a six - fold value into the gas chromatograph system, in which AsH_3 is adsorbed by a chromatographic column. After desorption AsH_3 enters into a double flame photometric detector. Due to the fact, that the light intensity emitted by AsH_3 is proportional to its concentration, the light signal is converted into electric signal. After amplifying and recording the arsenic content is calculated by using a calibration curve. The analytical system is shown schematically in Fig. 1.

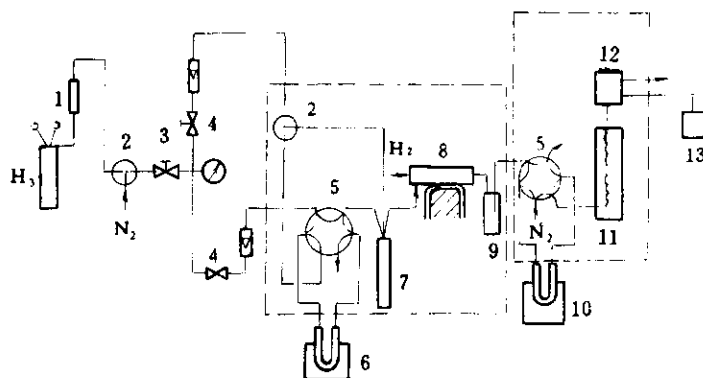


Fig. 1 Scheme of analytical system

- 1: absorbent 2: three-way valve 3: stabilizing valve 4: needle valve
 5: six way valve 6: absorption tube and low temperature bath 7: mixing chamber
 8: reduction furnace 9: trap for moisture 10: absorption column
 11: chromatographic column 12: double flame photometric detector 13: recorder

The operating parameters of the instrument are shown in Table 1.

Table 1 Operating parameters

Gas chromatographic system		Reduction system	
Detector temperature, °C	100	Reduction furnace temperature, °C	950
Separation column temperature, °C	130	Hydrogen flow speed, ml/min	160
Paper speed of recorder, ml/min	0.1	Nitrogen flow speed, ml/min	300
Carrier hydrogen flow speed, ml/min	60		
Flame hydrogen flow speed, ml/min	200		
Air(1) flow speed, ml/min	80		
Air(2) slow speed, ml/min	180		

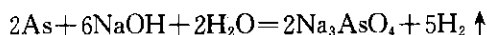
4 Sampling methods

Two sampling methods have been used according to the form of arsenide samples in tail gases. The solution absorption method can be used for sampling arsenides of different forms, where-

as the low temperature concentration method is much suitable for sampling gaseous arsenide (AsH_3) for its rapidness and simplicity.

4.1 Solution absorption sampling

Add absorption solution of 1% NaOH and 3% H_2O_2 to the sampler tube and then connect the sampler tube with the atmospheric sampler. Keep the gas flow speed at 0.3 L/min for 40 min. Pour the absorption solution into a quartz dish and dry it under an infrared lamp. The absorption reaction can be represented as;



4.2 Low temperature concentration sampling

Put the U-tube filled with chromatographic silica gel in a low temperature (-80°C) trap and then connect the U-tube with the atmospheric sampler. Keep the gas flow at a speed of 0.4 L/min for 30 min. Low temperature could be obtained by using a mixture of absolute ethyl alcohol and liquid nitrogen.

5 The detecting limit and error statistic

The minimum detecting limit is a measure of sensitivity of the method and can be expressed by formula: $D = 2Rn/S$, where Rn is the noise, S is the magnitude of the signal produced by the unit substance passing through detector (Zhan, 1983). The minimum detecting limit of the method is 0.01 ppm. The average deviation is 0.001 and the relative average deviation is 4.8%. The standard deviation is 0.0015 and the relative standard deviation is 6.2%.

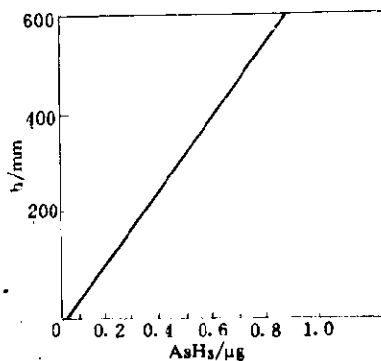


Fig. 2 Standard curve for AsH_3 (Filter 526 nm)

6 Establishment of standard curve for arsine

Prepare a standard gas mixture in which the concentration of AsH_3 is 0.87 $\mu\text{g}/\text{ml}$ and put separately 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of the standard gas mixture into the gas chromatography. Record the value of peak height and establish the dependence of peak height with arsine concentration (Fig. 2).

7 Comparison with spectrophotometry, plasma mass spectroscopy and atom absorption spectrometry

The analytical method for determination of arsenic has been compared with spectropho-

tometry, plasma mass - spectroscopy and atom absorption spectrometry. The results are shown in Table 2.

Table 2 shows that the data are coincident with each other. Using this method we analyzed the arsenic concentration in tail gases emitted from the vent tubes of an institute's building.

Table 3 shows that the method is very effective for assessment of the abatement process.

Table 2 Comparison of various methods for determination of As¹

Sample No.	Data obtained by various methods, mg/m ³				
	A	B	C	D	E
1	0.020	0.021			
2	0.459	0.460		0.457	
3	0.335	0.320		0.340	
4	0.122	0.120	0.130		0.130
5	0.160	0.140			
6	0.093	0.100			
7	0.050	0.062			
8	0.100	0.110			

¹Analyses were carried out by five different institutions using different methods A; represents this method; B, C; represent spectrophotometry; D; represents plasma mass spectroscopy; E; represents atom absorption spectrometry

Table 3 Arsenic concentration in tail gases from an institute's building, before and after abatement

Unit: $\mu\text{g}/\text{m}^3$

Sample No.	Analysis by this method		Analysis by spectrophotometry	
	Before	After	Before	After
1	0.459	0.016	0.460	0.014
2	0.180	0.480	0.230	0.040
3	0.120	0.020	0.130	0.025
4	0.160	0.020	0.140	0.022
5	0.093	0.032	0.100	0.038
6	0.100	0.020	0.110	0.040
7	0.310	0.040	0.320	0.004
8	0.007	0.004	0.005	0.004

8 Conclusion

The proposed gas chromatographic method being rapid, accurate and sensitive is capable to determine arsenic content in gaseous, liquid and solid samples. Its sensitivity and accuracy meet the requirement of microanalysis.

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