Determination of Trace Anions in High-Purity Gases in Semiconductor Processes

Wen Ruimei
Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

Abstract

This study involves testing for trace quantities of anions in high-purity gases (N_2, H_2, O_2, Ar, He, HCl, CO_2, NH_3, SiH_4, PH_3, and AsH_3) used in the electronics industry. A set of gas sampling devices is designed and constructed using membrane filtration (0.45 μm) in conjunction with solution absorption. In order to increase the detection sensitivity, the detection system was improved by using a large volume sampler (480 μL) instead of the conventional concentrator column. The ion chromatography method in this study is successful in determining F^-, Cl^-, NO^{3-}, HPO_4^{2-}, and SO_4^{2-} in 11 types of high-purity gases. This method is sensitive and accurate and meets the needs of anion-contamination control during the production of high-purity gases and very-large-scale integration processing.

Introduction

It is well known that high-purity gases are the fundamental materials widely used for very-large-scale integration (VLSI) processing for semiconductor technology. The most common high-purity gases are N_2, H_2, O_2, Ar, He, HCl, CO_2, NH_3, PH_3, SiH_4, and AsH_3. These gases contain traces of both metal and nonmetal impurities. Silicon wafers would be contaminated if these impurities enter the silicon wafers or their dioxide layers. Such contamination is adverse to the growth of epitaxial layer, oxidation, diffusion, and vapor-phase chemical deposition (1–4). In addition, the impurities in high-purity gases have a direct impact on the performance and yield of semiconductor materials and devices. For example, the residue of fluorine atoms of 10^{16}–10^{17} cm^{-2} on the surface of a silicon wafer is able to enhance the stacking faults in the epitaxial layer. The quality of the polysilicon, silicon nitride, and phosphorosilicate glass are degenerated by Cl^- contamination during chemical vapor deposition processing. Phosphorus in silicon wafers acts as an n-type impurity, and excess donors could be created if phosphorus contamination exists in a silicon wafer. Several researchers analyzed anions in atmospheric aerosols (5–6) by means of ion chromatography (IC). However, none have investigated the determination of anions in high-purity gases. In this study, IC has been successfully used for determining the impurity of F^-, Cl^-, NO_3^-, HPO_4^{2-}, and SO_4^{2-} in 11 types of high-purity gases. This method is sensitive and accurate and meets the needs of anion contamination control during the production of high-purity gases and VLSI processing.

Experimental

Equipment

The system used in this experiment consisted of a Dionex (Sunnyvale, CA) 2010i IC, a Dionex IonPac-AS4A anion separation column, a labratory-constructed large-volume sampler (480 μL), an AMMS-1 suppressor column, an IonPac 4G4A guard column, a conductivity cell, a cleaning table, a labratory-constructed gas sampling system, platinum and quartz crucibles, and membrane with a pore diameter of 0.45 μm.

Chemicals

All reagents, including NaF, NaCl, Na_2SO_4, $NaNO_3$, Na_2HPO_4, Na_2CO_3, $NaHCO_3$, HCl, and NaOH, were of super-pure grade or metal-oxide-semiconductor grade. The eluent solution was 0.075M $NaHCO_3$–0.2M Na_2CO_3. It should be diluted to 100 times its original volume with high-purity water before use. The regenerant solution was 1.25M H_2SO_4. It should also be diluted 100

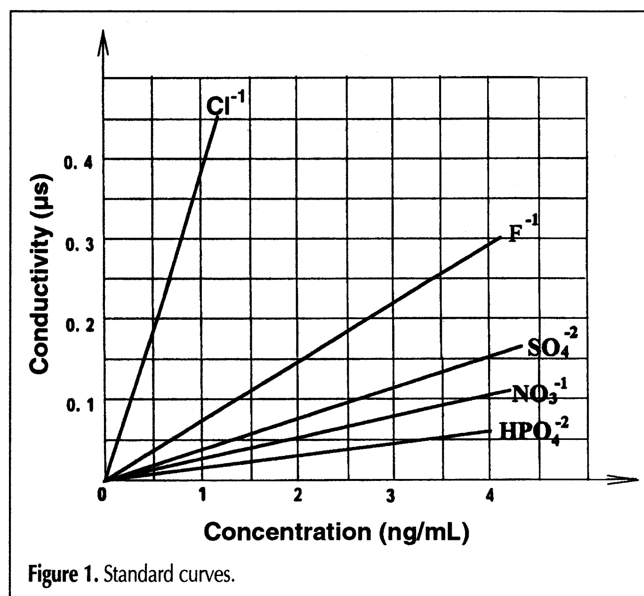

Figure 1. Standard curves.

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times with high-purity water before use. Standards were F^- (2 µg/mL), Cl^- (0.5 µg/mL), NO_3^- (10 µg/mL), HPO_4^{2-} (10 µg/mL), and SO_4^{2-} (5 µg/mL) solutions.

In order to obtain the standard curves, a certain amount of standard solution was diluted to form a solution series with the concentrations ranging from 0 to 200 µg/mL. The conductivity of various concentrations was measured by IC, and then the standard curves were plotted (Figure 1).

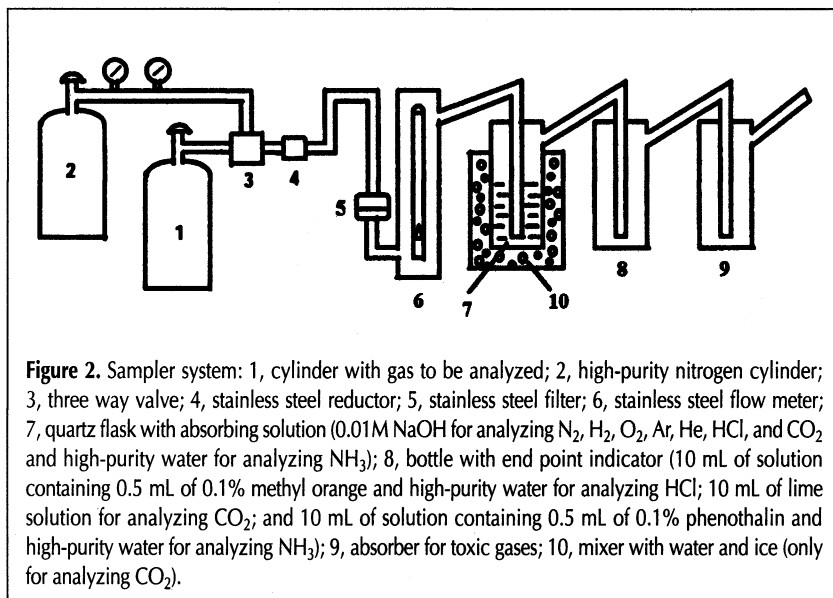

Figure 2. Sampler system: 1, cylinder with gas to be analyzed; 2, high-purity nitrogen cylinder; 3, three way valve; 4, stainless steel reductor; 5, stainless steel filter; 6, stainless steel flow meter; 7, quartz flask with absorbing solution (0.01M NaOH for analyzing N_2, H_2, O_2, Ar, He, HCl, and CO_2 and high-purity water for analyzing NH_3); 8, bottle with end point indicator (10 mL of solution containing 0.5 mL of 0.1% methyl orange and high-purity water for analyzing HCl; 10 mL of lime solution for analyzing CO_2; and 10 mL of solution containing 0.5 mL of 0.1% phenothalin and high-purity water for analyzing NH_3); 9, absorber for toxic gases; 10, mixer with water and ice (only for analyzing CO_2).

Sampling procedure

The sampling system designed for N_2, H_2, O_2, Ar, He, HCl, CO_2, or NH_3 is shown in Figure 2. Sampling systems should be operated under a ventilator. For CO_2 analysis, the quartz flask with the absorption solution was cooled with a mixture of water and ice.

A certain amount of PH_3, SiH_4, or AsH_3 was sampled using a teflon injector and transferred into 100 mL high-purity water that contains a small amount of alkaline. One-hundred microliters of diluted solution was taken out and then injected into the IC system.

In order to force out the air, the sampling system was purged with high-purity nitrogen for 10 min prior to sampling. The flow rate of N_2 was 100mL/min. The cylinder containing the analyte gas was switched on while turning off the N_2 cylinder. The flow rate of the analyte gas was set by adjusting valve 4 (Figure 2). The sampling conditions for the testing gases are listed in Table I (quantities are based on results of a large number of tests).

Analysis procedure

The sample gases were introduced into the IC system after sampling. The operation conditions are listed in Table II. After completing the sampling of N_2, H_2, O_2, Ar, or He, all of the absorbing solu-

Table I. Sampling Conditions for Various Gases

Gases	Volume of absorbing solution (mL)	Gas flow rate (mL/min)	Sampling duration (min)	Absorbing solution	Absorbed gas weight (g)	Comment
N_2, H_2, O_2, Ar, He	25	50	25	0.01M NaOH		
HCl	10	25	12	high-purity water	0.455	0.1% of methyl orange
CO_2	100	25	7	lime solution	0.32	turbid*
NH_3	10	75	8	high-purity water	0.54	0.1% of phenothalin

* Time needed for $Ca(OH)_2$ solution to turn turbid.

Table II. Operating Conditions

Separation column	Sensitivity of conductometer (µs)	Volume of sample (µL)	Eluent solution flow rate (mL/min)	Regenerating solution flow rate (mL/min)
IonPac-AS4A	1	100–480	3	2.8

* The working pressure is 600 psi for N_2, H_2, O_2, Ar, or He and 900 psi for other gases.

Table III. Error Statistics

	15 parallel samples containing 0.5 ng/mL Cl^-	15 parallel samples containing 5 ng/mL SO_4^{2-}	10 measurements for one sample containing 1 ng/mL Cl^-	10 measurements for one sample containing 10 ng/mL SO_4^{2-}
Average conductivity (ms/m)	0.24	0.19	0.50	0.41
Mean deviation	0.19	0.02	0.016	0.019
Standard deviation	0.025	0.027	0.02	0.021
Relative standard deviation (%)	10.6	14.1	4.0	5.1

Table IV. Results of Recovery Experiments

Tested gases	Analyzed anions	F^-	Cl^-	NO_3^-	HPO_3^-	SO_4^{2-}
Added quantity (ng)		10	50	50	10	10
Recovery (%)	HCl	81.6	–	98.7	100	105.5
Recovery (%)	CO_2	95.5	106.4	101.8	92.4	120.0
Recovery (%)	NH_3	91.2	–	108.3	107.6	113.4
Added quantity (ng)		4	4	10	10	6
Recovery (%)	N_2	94.6	103.6	98.5	109.2	99.0
Added quantity (ng)		5	3	10	10	10
Recovery (%)	SiH_4	86.5	94.5	103.3	94.0	108.7

Table V. Result of the Determination of Trace Anions from 11 Types of High-Purity Gases

	Anion concentrations in gases (ppb)										
Impurity	N_2	H_2	O_2	Ar	He	HCl	CO_2	NH_3	PH_3	SiH_4	AsH_3
F^-	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	25.7	11.0	16.2	< 0.2	4.4	14.0
Cl^-	1.6	0.8	1.3	3.5	0.6	–	94.8	–	49.8	138.0	15.2
NO_3^-	11.5	< 1.0	< 1.0	< 1.0	< 1.0	134.0	193.5	204.8	101.0	–	–
HPO_4^{2-}	< 0.2	< 1.0	< 1.0	< 1.0	< 1.0	28.6	19.5	32.4	–	86.0	< 1.0
SO_4^{2-}	2.4	1.2	< 0.2	2.0	1.1	18.0	8.6	14.5	33.0	50.0	31.5

Table VI. Impurity Anions Determined Using Different Sample Volumes

	Concentration of impurity anions (ppb)					
	N_2 (500 mL)	SiH_4 (500 mL)	N_2 (1000 mL)	SiH_4 (1000 mL)	N_2 (1500 mL)	SiH_4 (1500 mL)
F^-	< 0.2	4.2	< 0.2	4.4	< 0.2	4.0
Cl^-	1.5	125	1.6	136	1.4	128.0
NO_3^-	11.5	–	12.2	–	10.9	–
HPO_3^{2-}	< 0.2	85.0	< 0.2	84.6	< 0.2	87.9
SO_4^{2-}	2.5	49.0	2.4	47.3	2.1	50.1

Table VII. Effect of Type of Absorbing Solutions on Anion Determination

	Concentration of impurity anions (ppb)		
Analyzed anions	0.01M NaOH	0.01M NH_4OH	18 MΩ-cm High-purity water
Cl^-	1.4	1.0	0.6
NO_3^-	10.8	6.2	5.5
SO_4^{2-}	2.3	1.6	1.1

Table VIII. Comparison Among Various Sampling Methods

	Concentrations of anions (ppb)					
	Membrane filtration		Solution absorption		Membrane filtration with solution absorption	
Analyzed anions	N_2	SiH_4	N_2	SiH_4	N_2	SiH_4
Cl^-	1.0	87.0	1.4	96.5	1.6	138.5
SO_4^{2-}	1.8	35.4	2.0	39.6	2.4	50.1

tions were transferred into a platinum crucible and evaporated to dryness. The residue was dissolved in 2 mL water (18 MΩ-cm at 25°C) for analysis.

After completing the sampling of HCl, CO_2, or NH_3, the gas-absorbing solution should be immediately titrated with NaOH or HCl until the solution becomes neutral so that the sampling quantity of the test gas can be calculated. The absorbent solution was poured into a platinum crucible (for CO_2, a quartz crucible was used instead) and evaporated to dryness. The residual solid was dissolved in 5 mL of ultra-pure water for further analysis. High-purity N_2 (99.9999%) was used as a blank, and the purity of analyte nitrogen was ~ 99.999%.

The anion conductivities for both the blank and the analyte were measured using IC. After deducting the blank conductivity from the conductivity of the analyte, the anion concentrations of the analyte were obtained through comparison with the standard curves.

Error statistics

In order to check the precision and the accuracy of IC, repeated tests were carried out to derive error statistics. For example, 15 parallel samples with Cl^- concentrations of 0.5 ng/mL and 15 parallel samples with SO_4^{2-} concentrations of 5 ng/mL were used to measure the anion conductivity. In addition, one sample for Cl^- (taken from a Cl^- solution with a concentration of 1 ng/mL) and one sample for SO_4^{2-} (taken from an SO_4^{2-} solution with a concentration of 10 ng/mL) were tested 10 times for anion conductivity. Error statistics are shown in Table III. Table III shows that the values of relative standard deviation were small enough to satisfy the requirements for trace analyses.

Recovery experiments

Certain amount of F^-, Cl^-, NO_3^-, HPO_4^{2-}, and SO_4^{2-} were added to absorbing solutions, and the percentages of recovery were determined using the aforementioned analysis procedure during analysis of HCl, CO_2, NH_3, N_2, and SiH_4 using IC. The results are summarized in Table IV. It is clear that recovery is high and that the method used in this experiment to analyze anions is accurate.

Results and Discussion

The results of the determination of trace anions from 11 types of high-purity gases which are widely used in semiconductor processes are shown in Table V. It can be seen from Table V that the anions quantities in N_2, H_2, O_2, At, and He

were less than those in HCl, CO_2, NH_3, PH_3, SiH_4, and AsH_3.

Effect of sample volume

The concentration of anions in N_2 and SiH_4 were measured with three different sample volumes. The results are listed in Table VI. It was found that sample volume varying from 500 to 1500 mL did not effect the determination of anions in gases.

Effect of kinds of absorbing solutions

The effect of different types of absorbing solutions (i.e., 0.01M NaOH, 0.01M NH_4OH, and high-purity water) on the determination of anions in N_2, H_2, O_2, At, and He was studied. The concentrations of anions were detected, and the results appear in Table VII. The results show that the best solution for absorption the gases is NaOH (0.01M).

Effect of sampling methods

In Table VIII, the concentrations of Cl^- and SO_4^{2-} in N_2 and SiH_4 are listed using different sampling methods (i.e., membrane filtration, solution absorption, and membrane filtration with solution absorption).

Table VIII shows that both membrane filtration with a pore diameter of 0.45 µm and solution absorption gave low results. This was due to the loss of samples. However, a new sampling method was developed (i.e., membrane filtation with a pore diameter of 0.45 µm and solution absorption) which gave satisfactory results.

Conclusion

An IC method has been established for determining F^-, Cl^-, NO_3^-, HPO_4^{2-}, and SO_4^{2-} in high-purity gases such as N_2, H_2, O_2, Ar, He, HCl, CO_2, NH_3, SiH_4, PH_3, and AsH_3. The method is sensitive and accurate and meets the needs of anion-contamination control during the production of high-purity gases and VLSI processing.

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