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Application of ion chromatography to the semiconductor industry

I. Measurement of acidic airborne contaminants in cleanrooms

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Abstract

The purpose of this study is to establish an analytical method for the simultaneous measurement of various acidic airborne contaminants in class 1 cleanrooms of a semiconductor fabrication facility (Fab). Acidic contaminants in air samples were adsorbed on silica gel tubes, extracted with carbonate–hydrogencarbonate solutions, and analyzed by ion chromatography. The recovery of HF was 100% and that of HCl was 91~100%. The method shows high resolution and sensitivity, and is capable for air analysis in the class 1 cleanroom. Different locations inside the cleanroom show deviations in the contaminant levels, indicating that the air quality is not the same throughout the cleanroom. The wet chemical station shows higher levels of contaminant concentrations than the other two areas. Each location also shows day-to-day variation. © 1998 Elsevier Science B.V.

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1. Introduction

Manufacturing semiconductor integrated circuits has become a state-of-the-art technology in the last few decades. As new science and technology develops, the critical dimension of the device decreases to below 0.35 μm . In the fabrication of such sub- μm geometry, it is of utmost importance to control its manufacturing in a “contaminant-free” environment. Otherwise, device failure occurs and product yield decreases as a result of the unintended deposition of contaminants on the wafer surface, growth of native oxide, blockage of critical line, corrosion of process tool, etc., [1]. In the 1980s utility impurity of 100–1000 parts per billion (ppb) was sufficient for the feature size of 2 μm . Today, utility impurity of 1 ppb is required for 0.35 μm devices [2]. As important as the technology of improving cleanliness is, precise

and reliable analytical techniques are also essential. The measurement and control of contaminants are required in all areas related to the wafer fabrication process. Lin et al. [3] developed an analytical method for measuring ppt levels of anions and cations in ultrapure water by on-line ion chromatography (IC). Trace anions in concentrated acids can be determined by IC with appropriate sample pretreatment [4,5]. Air quality in the cleanroom, however, has not received as much attention as process chemicals. For example, SEMI has not published guidelines for airborne contaminants in a cleanroom; only classification of airborne contaminant levels is available [6].

Many methods of measuring indoor air quality were established for safety and health reasons. Patnaik [7] summarized US National Institute for Occupational safety and Health (NIOSH), US Environmental Protection Agency (EPA) and other methods for air analysis. The analytical methods for

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inorganic acidic contaminants include titrimetry, colorimetry, gravimetry, ion-selective electrode methods and IC. The titrimetric method suffers from interference with other ions present in the sample. The colorimetric and gravimetric determinations do not give accurate results at concentrations below 250 mg/l (the contaminant levels in cleanroom are much lower than that). The ion-selective electrode method determines a single component and is not sensitive enough for air analysis in cleanrooms. IC, on the other hand, seems to be a promising technique for its capability for simultaneous measurement of multiple compounds at trace levels. One of the official methods described how chloride in air is sampled using a midjet impinger containing 0.5 M sodium acetate [8]. Cassinelli et al. [9,10] collected inorganic acids in air using a silica gel tube and quantified by IC. That method was included in NIOSH methods [11]. This paper demonstrates an appropriate sample collection method to measure acidic airborne contaminants in cleanrooms by IC. Air samples in different locations of the cleanroom were also analyzed.

2. Experimental

2.1. Reagents

The purity of the chemicals and reagents is extremely important for trace analysis. High purity water of 18.2 M Ω cm was obtained from a class 1 semiconductor fabrication facility in Taiwan. Fig. 1 shows the IC chromatograms of the high purity water and eluent prepared from this water. Analytical-grade sodium fluoride, sodium chloride (Shimadzu, Osaka, Japan), sodium bromide, sodium nitrite, sodium nitrate (Yakuri, Osaka, Japan), potassium sulfate and potassium phosphate (Nihon Shiyaku, Osaka, Japan) were used for preparation of standard solutions. Eluent for IC analysis was a buffer solution of 1.7 mM of NaHCO₃ and 1.8 mM of Na₂CO₃ (Fisons Scientific, Loughborough, UK).

2.2. Sampling

Silica gel sorbent tubes (Supelco ORBO-53, Bellefonte, PA, USA) were used in the collection of

inorganic acids in cleanroom air. The tube was a glass tube (11 cm \times 7 mm O.D.) containing two sections of silica gel. Each front section had 400 mg of silica gel and the back-up section, 200 mg. A urethane foam plug was inserted between these two sections and at the other end of the back-up section. A thick glass fiber filter was placed in front of the front section to collect particulate and/or aerosol components, if present. Prior to sampling, the flow meter (Model B-125-40, Porter Instruments, Hatfield, PA, USA) was calibrated with a bubble meter (Supelco). Fig. 2 shows the diagram of air sampling. Air samples were drawn by an air pump (Hiblow, Model SPP-15GA, Techno Takatsuki, Osaka, Japan). The flow-rate was adjusted at 0.216 l/min by a precision valve on the flow meter. After 24-h sampling, the ends of the tube were sealed with the original plastic cap and the tube was returned to the laboratory for analysis. The front and the back-up sections of silica gel were placed in separate centrifuge tubes (Supelco). Eluent (10 ml) was added to each centrifuge tube and the tube was heated in boiling water bath for 10 min to desorb the analytes. Upon cooling, the solution was filtered and injected onto the IC system for analysis.

Midget impingers were also used in sampling for comparison with the results by silica gel sorbent tubes. Two impingers (Supelco) were filled with 7 ml of IC eluent and connected in series. The air was bubbled through the collection solution at 0.2 l/min. After 24-h sampling, the solution was filtered and injected onto the IC system for anion analysis.

Air samples were taken at three locations in a class 1 cleanroom: the wet chemical station, the bay and the photolithography area. Blanks were analyzed along with the air samples and the results were corrected by subtracting the blank.

2.3. Chromatographic procedure

Analyses were performed on a suppressor-type IC (DX-100, Dionex, Sunnyvale, CA, USA). The eluent was pumped at a flow-rate of 2 ml/min. A 500- μ l sample aliquot was injected into the instrument. An analytical column IonPac AS4A-SC (250 mm \times 4 mm, Dionex), with a guard column (AG4A, 50 mm \times 4 mm), was used in the measurement. Following the analytical column was an anion self-re-

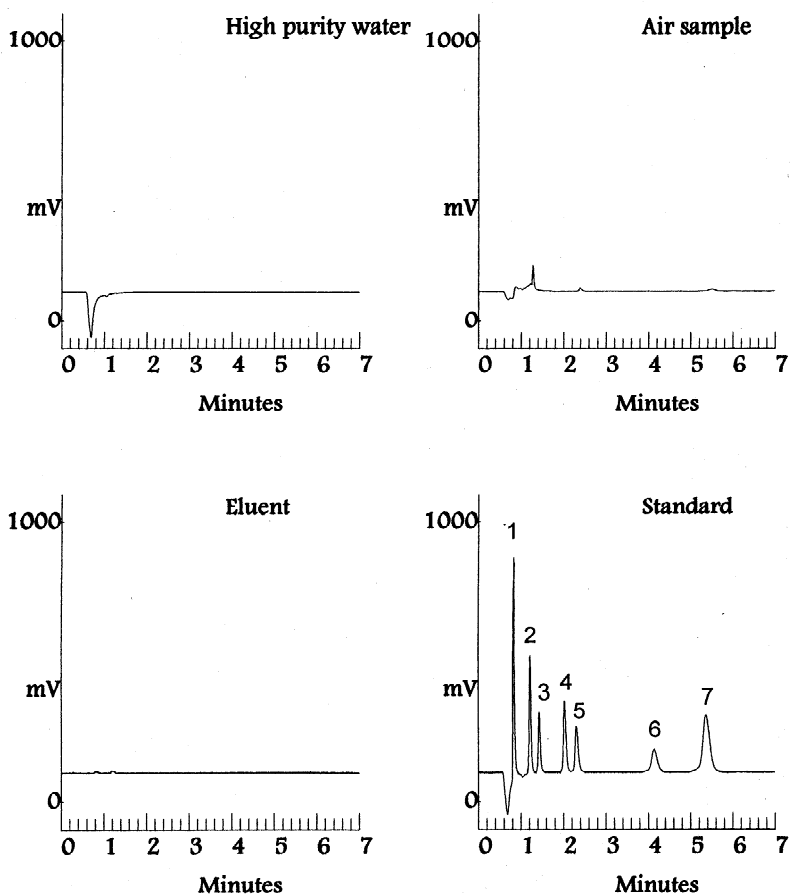


Fig. 1. IC chromatograms of high purity water, eluent, sample and standard. Peaks: 1=fluoride, 2=chloride, 3=nitrite, 4=bromide, 5=nitrate, 6=phosphate, 7=sulfate.

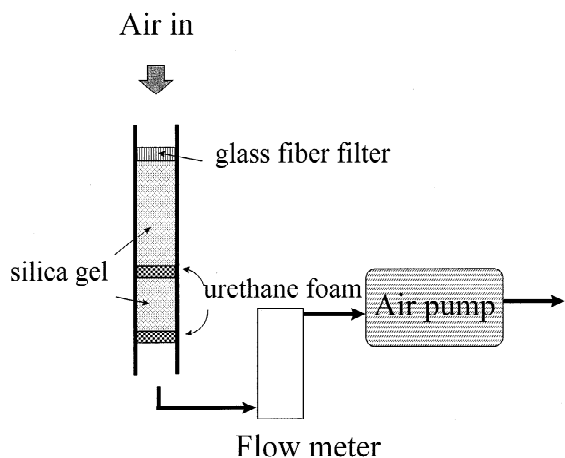


Fig. 2. Diagram of air sampling by silica gel tube.

generating suppressor (ASRS) using the recycle of the eluent as a regenerant. A conductivity cell was used as the detector for measuring suppressed conductivity. The conductivity output was sent to an Advanced Computer Interface (ACI, Dionex) and to a computer through an RS-232 cable. The AI-450 software (Dionex) in the computer performed the tasks of equipment control, signal receiving, calibration, integration, data processing and printing control.

2.4. Calibration

A five-level calibration was utilized in the analysis. The standards containing 0.05, 0.125, 0.25, 0.5 and 1.0 mg/l of each analyte were prepared. The

calibration curves were generated using the least squares method.

3. Results and discussion

The calibration curves show excellent linearity of responses. The coefficients of determination (R^2) in the regression lines range from 0.992 to 0.998. Table 1 shows the reproducibility on one solution of known concentration ($n=5$). The relative standard deviations (R.S.D.s) ranged from 1.7% to 6.6%.

The scrubbing solution and impingers were first used for air sampling. When the air sampling rate was greater than 0.5 ml/min, bubbling of the solution was so severe that too much solution in the first impinger escaped into the second impinger, resulting in a significant decrease (~50%) of the solution. Even at a reduced flow-rate of 0.2 ml/min, the scrubbing solution still decreased by 30% due to the volatility of the solution. Other collection solutions, such as water and 0.1 M NaOH, had the similar difficulty. Therefore, the sampling flow-rate was set at 0.2 l/min for 24 h and the results were corrected by the final solution volume after sampling. Table 2 shows the results using the impingers. The results show that hydrochloric and sulfuric acid were the most dominant acidic contaminants in the cleanroom. However, no hydrofluoric acid (HF) was detected in the impinger method probably due to the fluoride interaction with the glass material of the impingers [10].

The lack of hydrofluoric acid by the impinger sampling lead to an alternative method of air sampling. Silica gel is a good choice because it adsorbs inorganic acids very well and the adsorbed hydrofluoric acid can be extracted by an appropriate solution, such as sodium carbonate–sodium bicarbonate mixture. The silica gel tubes, then, was used

Table 2

Airborne acidic contaminants in class 1 cleanroom by impinger sampling

Acid concentration (nmol/m ³)	Site 1 ^a	Site 2 ^b	Site 3 ^c
Hydrofluoric acid	0	0	0
Hydrochloric acid	484	221	264
Nitric acid	490	143	61
Sulfuric acid	1243	231	209

^a Wet chemical station.

^b Bay area.

^c Lithophotography area.

Air flow-rate: 0.2 l/min, sampling time: 24 h, scrubbing solution: 7 ml of sodium carbonate–sodium hydrogencarbonate (1.8 mM:1.7 mM) solution.

for sampling at a flow-rate of 0.2 l/min for 24 h. Table 3 shows the results at the wet chemical station and the bay area. In contrast to the impinger sampling, the hydrofluoric acid was detected by the silica gel sampling. Its concentration ranged from 280 to 530 nmol/m³, as shown in Table 3. Furthermore, the

Table 3

Airborne acidic contaminants in class 1 cleanroom by silica gel sampling

Date	Acid concentration (nmol/m ³)	Site 1 ^a	Site 2 ^b
7–8 August 1997	Hydrofluoric acid	526	284
	Hydrochloric acid	668	619
	Nitric acid	154	0
	Sulfuric acid	956	349
13–14 August 1997	Hydrofluoric acid	296	283
	Hydrochloric acid	104	59
	Nitric acid	163	0
	Sulfuric acid	117	0

^a Wet chemical station.

^b Bay area.

Air flow-rate: 0.2 l/min, sampling time: 24 h.

Table 1

Reproducibility of IC analysis ($n=5$)

Analyte	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
Mean (mg/l)	0.200	0.339	0.247	0.528	0.219	0.407	0.566
S.D. (mg/l)	0.012	0.01	0.006	0.009	0.005	0.027	0.016
R.S.D. (%)	5.9	2.9	2.6	1.7	2.2	6.6	2.8

Table 4
Recovery of acidic components adsorbed on silica gel tubes

Analyte	Wet chemical station		Photolithography area	
	Front ^a	Back-up ^b	Front	Back-up
HF (nmol/m ³)	917	ND ^c	534	ND
Recovery	100%		100%	
HCl (nmol/m ³)	513	45	178	ND
Recovery	91%		100%	

^a Analyte in the front section of silica gel tube.

^b Analyte in the back-up section of silica gel tube.

^c Not detectable.

two-section silica gel tubes enable us to study the collection efficiency of the silica gel. By analyzing these two sections, it is possible to calculate the recovery of the sampling devices. Table 4 shows the concentrations of analytes adsorbed on the individual silica gel sections. It shows that the collection efficiency is ~100% for HF and 91~100% for HCl. This concludes that IC eluent as a desorption solution for silica gel was adequate and it recovered acidic analytes completely. Besides, silica gel tube is recommended for one more reason: it is convenient in small area sampling (e.g., in wafer storage cassette or mini-environment) and can be used with personal pump for sampling in movement. Figs. 3–5 show the concentration of inorganic acids (in nmol/m³) at

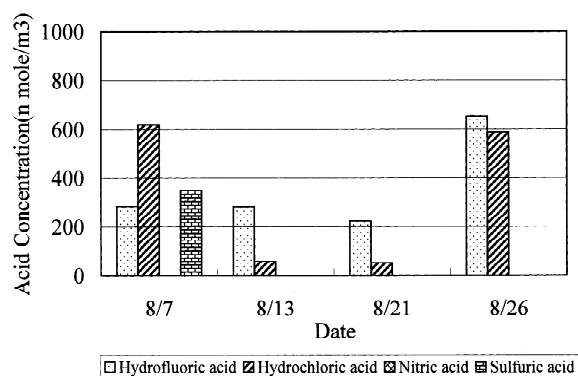


Fig. 4. Concentrations of acidic contaminants at the bay area.

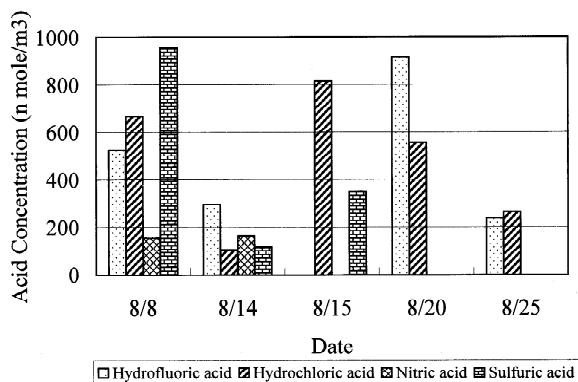


Fig. 3. Concentrations of acidic contaminants at the wet chemical station.

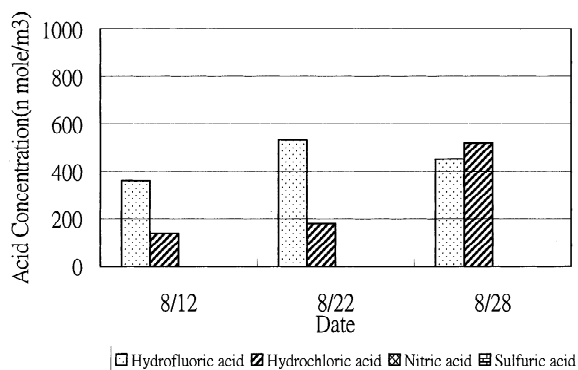


Fig. 5. Concentrations of acidic contaminants at the photolithography area.

three locations in the class 1 cleanroom. It appeared that the wet chemical station tended to have higher levels of acid contaminants which is probably due to the vaporized acids used in wafer cleaning and rinsing in that particular area.

4. Conclusions

The acidic contaminants in cleanroom air can be concentrated on silica gel, subsequently desorbed by carbonate–bicarbonate solution and analyzed by IC. The method is sensitive and recovers acidic airborne contaminants very well. Air analysis in the class 1 cleanroom indicates that the air quality is not the same throughout the cleanroom. Process tools and process chemicals are potential sources of contamination. Furthermore, the results show day-to-day variation. The air quality in the cleanroom is not as clean and stable as one thinks and it needs to be controlled in order to improve the wafer yield and performance.

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