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Applications of ion chromatography in the semiconductor industry II. Determination of basic airborne contaminants in a cleanroom

S. Jessie Lue*, C. Huang

Department of Chemical Engineering, Chang Gung University, Kwei-Shan, Taoyuan County, Taiwan

Abstract

Since the geometry of semiconductors and integrated circuits has been shrunk to well below sub-micron dimensions, there is a great demand for precise and reliable analytical techniques to measure and monitor the contaminants in all areas related to the fabrication process. Special concerns about the air cleanliness in a Fab lead to the necessity for developing analytical techniques to perform this task. In this research, basic airborne contaminants in a cleanroom were adsorbed onto a collection tube, subsequently extracted with deionized water and analyzed by ion chromatography. Such a method is capable of simultaneously measuring the concentrations of ammonia and cations (e.g., sodium, potassium, calcium, magnesium, etc.) present in the cleanroom air samples. The optimal sample preparation method was determined and the analyte concentrations at various locations in the cleanroom were measured. The results showed significant variations from one location to another. The long-term fluctuations in the contaminant levels were also significant. Data obtained using this method compared well with data from inductively coupled plasma analysis of the same materials. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Semiconductors; Air analysis; Inorganic cations; Basic contaminants; Trace analysis; Manufacturing; Cleanroom

1. Introduction

In the fabrication of the sub-micron semiconductor integrated circuit, it is of the utmost importance to control its manufacturing in a ''contaminant-free'' environment. The cleanliness of a fabrication facility (Fab) for making state-of-the-art semiconductors needs to be strictly controlled. Otherwise, device failure occurs and product yield decreases [1]. The photolithography process is especially sensitive to airborne contaminants [2]. To ensure product quality, SEMI (Semiconductor Equipment and Material International) has published quality specifications for

process chemicals and high purity water for wafer processing. For the air quality in a cleanroom of a Fab, only classifications for airborne contaminant levels are available. Four categories of airborne molecular contaminants, including acids (A), bases (B), condensables (C) and dopants (D) have been identified in SEMI F21 [3]. Classification is defined as the maximum total gas phase concentrations in parts per trillion molar (pptm) and expressed as M?-I, where ? is the category of contaminant (A, B, C or D) and I equals to 10^n with n being an integer. For example, a cleanroom with total acidic airborne contaminant concentrations of 100–1000 pptm meets the MA-1000 criterion.

Many analytical methods are being developed to determine the type and concentrations for contaminants in Ultrapure water [4] and process chemicals

*Corresponding author. Tel.: +886-3-328-3016, ext. 5389; fax: +886-3-328-3031.
E-mail address: jessie@mail.cgu.edu.tw (S.J. Lue)

[5,6]. Air analysis for a cleanroom, however, has not progressed much and the research in this field is very limited. Lue et al. [7] recently developed a method employing silica gel sorbent to trap the acidic contaminants in cleanroom ambient air and analyzed the captured contaminants with ion chromatography (IC). Yabumoto and Tanaka [8] used impingers and trace analyzers such as graphite furnace atomic absorption spectroscopy, inductively coupled plasma mass spectrometry (ICP-MS) and IC to measure anions and cations from cleanroom air and gases. In this research the objective was to establish a method for the simultaneous measurement of trace amount of basic airborne contaminants, including ammonia, alkali and alkaline earth metal cations. Other goals included the investigation of the optimal sample pretreatment condition and a determination of contaminant collection efficiency. Meanwhile, a correlation between the cation data from this method and the data obtained from ICP analysis of the same materials was determined.

2. Experimental

2.1. Reagents

The purity of the chemicals and reagents is extremely important for trace analysis. High purity water of 18.2 MΩ cm was obtained from a class 1 semiconductor fabrication facility in Taiwan. Analytical-grade sodium chloride (Fisons, Loughborough, UK), ammonium chloride, magnesium chloride, calcium chloride, potassium chloride (Yakuri, Osaka, Japan) were used for the preparation of standard solutions. Eluent for IC analysis was a mixture solution of 5 mM of sulfuric acid (Nihon Shiyaku, Osaka, Japan) and acetonitrile (ALPS Chemicals) (91:9, v/v). Fig. 1 shows the chromatogram of a standard solution.

2.2. Sampling

Sulfuric acid-treated silica gel sorbent tubes (Supelco ORBO-554, Bellefonte, PA, USA) were used in the collection of basic contaminants in cleanroom air. Prior to sampling, the flow-rate of a battery-operated personal air pump (Buch I.H. pump, Supelco) was calibrated with a bubble meter (Supelco). Air samples were drawn using the personal pump at a predetermined flow-rate, ranging from 50 to 100 ml/min. After sampling, the ends of the tube were sealed with the original plastic caps, wrapped with Parafilm (American National Can, Chicago, IL, USA) and the tube was returned to the laboratory for analysis. Then the silica gel was
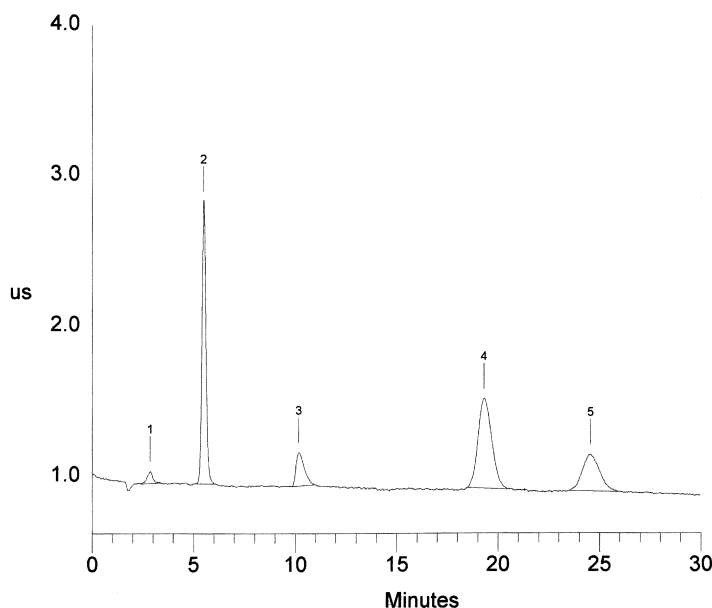

Fig. 1. IC chromatogram of a standard solution. Peaks: 1=Sodium, 2=ammonia, 3=magnesium, 4=calcium, 5=potassium.

placed in a nitric acid-cleaned test tube (concentrated HNO_3 obtained from Shimakyu, Osaka, Japan). Fifteen milliliters of deionized (D.I.) water was added to the test tube. The tube was capped and placed in an ultrasonic water bath (Bransonic 5210, Danbury, CT, USA) for 45 min to desorb the analytes [9]. Upon cooling, the solution was filtered and injected into the IC system for analysis.

Air samples were taken at three locations in a cleanroom. Blanks were analyzed along with the air samples and the results were corrected by subtracting the blank. Two determinations were made for each extract solution and the average was reported.

2.3. Chromatographic procedure

Analysis was performed on a suppressor-type IC system (DX-100, Dionex, Sunnyvale, CA, USA). The eluent was pumped at a flow-rate of 1.2 ml/min. A 500-μl sample aliquot was injected into the instrument. The analytical column IonPac CS15 (250 mm×4 mm, Dionex), with a guard column (CG15, 50 mm×4 mm, Dionex), was used in the measurement. Following the analytical column was a cation self-regenerating suppressor (CSRS-II, Dionex) using external D.I. water as a regenerant. The water regenerant was pumped at a flow-rate of 5 ml/min with a peristaltic pump (Eyela Rikakikai, Tokyo, Japan). 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.

A four-level calibration was utilized in the analysis. The standards containing 0.1, 0.5, 1.0 and 2.0 mg/l of each analyte were prepared. The calibration curves were generated using the least-squares method.

2.4. Determination by inductively coupled plasma

The desorbed aqueous solutions were also analyzed by ICP-atomic emission spectroscopy (AES, Model PS-1000, Leeman Labs., Lowell, MA, USA). The sample was delivered using a peristaltic pump at a flow-rate of 1.0 ml/min and the argon flow was maintained at 15 l/min. The nebulizer pressure was 44 p.s.i. and the electrical power for plasma was 1 kW (1 p.s.i.=6894.76 Pa). The wavelengths used for quantification were 589.592 nm (Na), 279.553 nm (Mg), 393.366 (Ca), and 766.49 nm (K), respectively. Standard solutions at concentration of 0.01, 0.5, 1, 5 and 10 μg/l were used to calibrate the instrument prior to analysis. The concentration of each sample was determined three times and the average was reported.

3. Results and discussion

As indicated in SEMI F21, the critical basic contaminants in a cleanroom air include ammonia and amines [3]. The sulfuric acid-treated silica gel tube was chosen to collect these contaminants for its capability to adsorb both ammonia and amines. The analytical column CS15 was used since it resolves well the amine peaks from monovalent and divalent cation peaks [10].

In the four-level calibration of IC, the calibration curves all showed excellent linearity on responses, with the coefficients of determination (R^2) in the regression lines ranging from 0.992 to 0.996.

In order to determine the optimal sampling condition, sampling time and flow-rate were changed one at a time. The flow-rate of 100 ml/min was first used as the recommended sampling rate in the NIOSH method [9], which describes the sampling procedure for measuring ammonia in air samples. Fig. 2 shows the contaminant concentrations determined at this air flow-rate with sampling time of 10–120 min. It was noted that ammonia and potassium were the dominant contaminant species and no amines were found. It was also noted that the contaminants were trapped efficiently on the sorbent in the first 10 min, and decreased dramatically with greater sampling time. This may be due to a saturated or partially saturated sorbent surface after quick adsorption of the alkali analytes on the acid-treated sorbent. The sorbent reached a point at which it could not trap much more analytes. It seems that the sampling device favors a shorter sampling time. If the sampling period is extended to long, the analytes are not efficiently adsorbed onto the collection tube and the results are inaccurate.
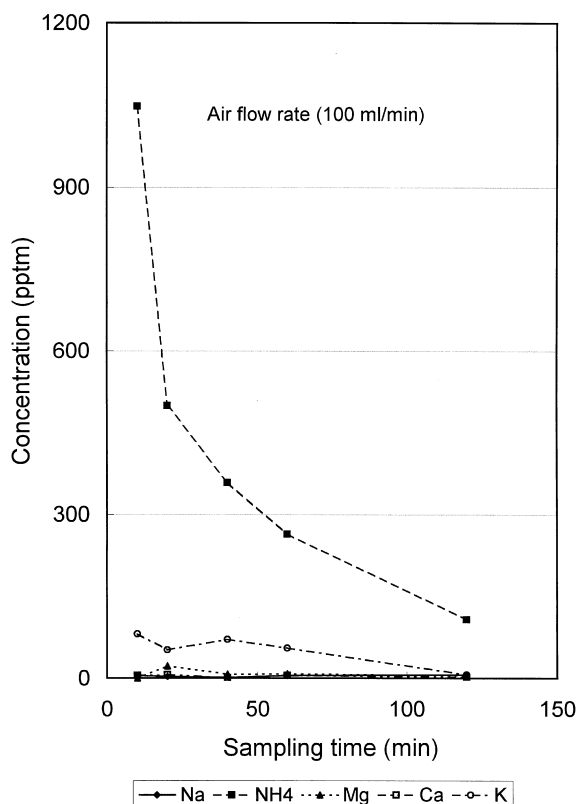
Fig. 2. Effect of sampling time on the results for basic contaminants at a flow-rate of 100 ml/min.

Fig. 3. Effect of sampling flow-rate on the results for basic contaminants at a total sample volume of 1 l.

Second, the air was collected at various flow-rates with a sample volume of 1 l. Three sets of experiments were performed: 50 ml/min for 20 min, 75 ml/min for 13.3 min, and 100 ml/min for 10 min. Fig. 3 indicates that the concentrations sampled at 75 ml/min and 100 ml/min did not differ significantly. However, the sample at 50 ml/min showed higher results with the exception of sodium. It is well known that for air sampling with sorbent, there is an upper limit for air flow-rate. If the limit is exceeded, a breakthrough will occur and not all of the analytes are absorbed. So a lower flow-rate is preferred in most cases. However, an extended sampling time associated with a lower sampling rate may result in adverse effects (such as sample loss and artifacts from reactions between absorbed analytes) on air sampling. To minimize these potential drawbacks and to expedite the sampling procedure, a flow-rate of 50 ml/min was chosen in the following analyses.
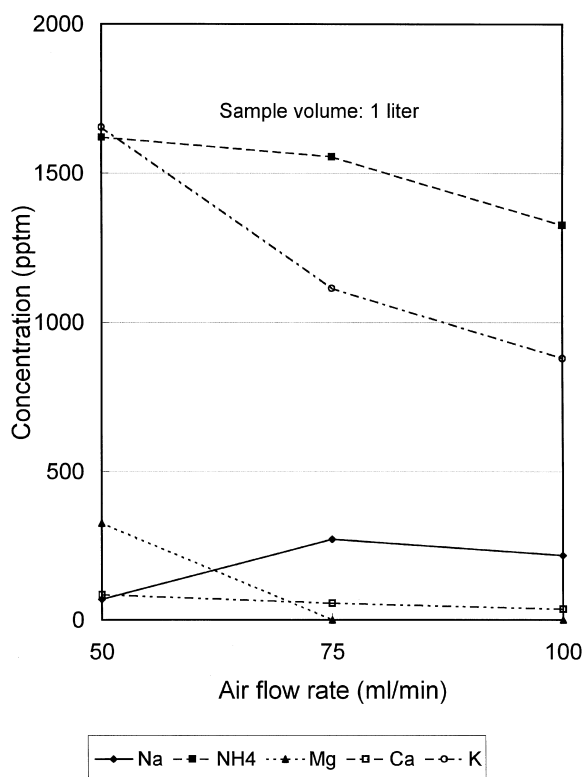
The collection efficiency of the sorbent was determined after spiking the sorbent with known concentrations of analytes. The efficiency was between 81% (for potassium) and 90% (for ammonia). Table 1 shows the 8-h concentration variation of basic airborne contaminants at three locations in the cleanroom. Ammonia and potassium levels were significantly different between locations Y and F, and the other contaminants were of similar levels in an

Table 1
Contaminant concentrations at different locations in a cleanroom within an 8-h period

Analyte	Location Y	Location F	Location E
Na^+	385 ± 52[a]	305 ± 12	341
NH_4^+	1800 ± 286	1305 ± 69	1080
Mg^{2+}	2743 ± 247	2622 ± 199	1961
Ca^{2+}	48 ± 33	72 ± 37	50
K^+	2417 ± 215	1769 ± 155	893

[a] Mean±standard deviation, in pptm.

Table 2
The concentrations of basic airborne contaminants at location E sampled 15 days apart

Analyte	Concentration (pptm)	
	8 July	24 June
Na^+	349	69
NH_4^+	794	1621
Mg^{2+}	1906	326
Ca^{2+}	36	85
K^+	866	1655

Table 3
Calcium comparison using IC and ICP-AES analytical methods

Sample no.	Result using IC ($\mu g/l$)	Result using ICP-AES ($\mu g/l$)
1	0.29	0.21
2	0.14	0.12
3	0.11	0.11

8-h period. All three locations had one thing in common: K^+, Mg^{2+} and NH_4^+ were the major contaminants and concentrations of Na^+ and Ca^{2+} were negligible compared to the others.

To investigate the long-term variations in airborne contaminant levels, location E was sampled two times, 15 days apart. Table 2 indicates that the long-term variation is quite large, even showing a 100% variation for many contaminants.

In order to compare the data from IC and ICP-AES determinations, same samples were analyzed with these two methods in parallel. In the five-point calibration curves of ICP-AES, the coefficients of determination (R^2) all exceeded 0.999. As indicated in Table 3, excellent agreement between the two techniques was obtained. The cation concentrations from these methods showed high correlation coefficients of 0.94–0.996.

4. Conclusions

In this research, IC was used to measure the concentrations of ammonia and cationic contami- nants in cleanroom air after the analytes were absorbed onto sulfuric acid-treated silica gel and extracted with D.I. water. An analytical column CS15 was used and the mixture H_2SO_4–acetonitrile was used as the eluent at 1.2 ml/min. Ammonia, alkali and alkaline earth cations were simultaneously measured. Data obtained using this method com- pared well with the data from ICP analysis of the same materials. Air analysis at different locations in the cleanroom indicated that the air quality is not the same throughout the cleanroom. However, potas- sium, ammonia, magnesium are the dominant con- taminant species. Furthermore, the results show severe long-term variations in the contaminant levels in cleanroom ambient air. The air quality in the cleanroom is not as clean and stable as one would think and needs to be controlled in order to improve wafer yield and performance.

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