This article was downloaded by: [National Chiao Tung University 國立交通大學]
On: 30 April 2014, At: 01:27
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of the Air & Waste Management Association
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uawm20

Inorganic Acid Emission Factors of Semiconductor Manufacturing Processes

HungMin Chein [a], Tzu Ming Chen [a], Shankar Gopala Aggarwal [a], Chuen-Jinn Tsai [b] & Chun-Chao Huang [b]

[a] Center for Environmental, Safety, and Health Technology Development, Industrial Technology Research Institute, Hsin-chu, Taiwan

[b] Institute of Environmental Engineering, National Chiao Tung University, Hsin-chu, Taiwan

Published online: 21 Feb 2012.

To cite this article: HungMin Chein, Tzu Ming Chen, Shankar Gopala Aggarwal, Chuen-Jinn Tsai & Chun-Chao Huang (2004) Inorganic Acid Emission Factors of Semiconductor Manufacturing Processes, Journal of the Air & Waste Management Association, 54:2, 218-228, DOI: 10.1080/10473289.2004.10470898

To link to this article: http://dx.doi.org/10.1080/10473289.2004.10470898

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **54**:218–228
Copyright 2004 Air & Waste Management Association

Inorganic Acid Emission Factors of Semiconductor Manufacturing Processes

HungMin Chein, Tzu Ming Chen, and Shankar Gopala Aggarwal
Center for Environmental, Safety, and Health Technology Development, Industrial Technology Research Institute, Hsin-chu, Taiwan

Chuen-Jinn Tsai and Chun-Chao Huang
Institute of Environmental Engineering, National Chiao Tung University, Hsin-chu, Taiwan

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

ABSTRACT
A huge amount of inorganic acids can be produced and emitted with waste gases from integrated circuit manufacturing processes such as cleaning and etching. Emission of inorganic acids from selected semiconductor factories was measured in this study. The sampling of the inorganic acids was based on the porous metal denuders, and samples were then analyzed by ion chromatography. The amount of chemical usage was adopted from the data that were reported to the Environmental Protection Bureau in Hsin-chu County according to the Taiwan Environmental Protection Agency regulation. The emission factor is defined as the emission rate (kg/month) divided by the amount of chemical usage (L/month). Emission factors of three inorganic acids (i.e., hydrofluoric acid [HF], hydrochloric acid [HCl], and sulfuric acid [H_2SO_4]) were estimated by the same method. The emission factors of HF and HCl were determined to be 0.0075 kg/L (coefficient of variation [CV] = 60.7%, n = 80) and 0.0096 kg/L (CV = 68.2%, n = 91), respectively. Linear regression equations are proposed to fit the data with correlation coefficient square (R^2) = 0.82 and 0.9, respectively. The emission factor of H_2SO_4, which is in the droplet form, was determined to be 0.0016 kg/L (CV = 99.2%, n = 107), and its R^2 was 0.84. The emission profiles of gaseous inorganic acids show that HF is the dominant chemical in most of the fabricators.

IMPLICATIONS

Emission factors of inorganic acids for semiconductor manufacturing are required in Taiwan to determine the air pollution fee and initiate its collection from factories. The emission profile also is needed to better understand the industrial air pollution problems. Therefore, Hsin-chu County has performed an investigation project to study the characteristics of industrial inorganic acid emissions.

INTRODUCTION
According to the "Air Pollution Regulation and Emission Standard for the Semiconductor Manufacturing Industry (APRESS)" rectified and issued by the Taiwan Environmental Protection Administration (TEPA) in April 1999,[1] the semiconductor manufacturing industries are defined as those who engage in integrated circuit (IC) wafer production, wafer package, epitaxial, photo-mask production, and wire frame production. Semiconductor manufacturing industries contribute significantly to economic growth and have become the most important industry in Taiwan. However, the emission of hazardous air pollutants (HAPs) produced by the industries increasingly is deteriorating the ambient air quality. An emission factor is a representative value that attempts to relate the quality of a pollutant released to the atmosphere with an activity associated with the release of that pollutant.[2] The "Compilation of Air Pollutant Emission Factor, AP-42" details the most complete list of emission factors from various industries, including the emission factors of total organic compounds (TOCs), volatile organic compounds (VOCs), methane (CH_4), ethane (C_2H_6), and other kinds of organic and inorganic compounds. A specialty conference (i.e., "Emission Inventory: Regional Strategies for the Future") was held in 1999 sponsored by the Air & Waste Management Association (AWMA) and the U.S. Environmental Protection Agency to discuss the application of the emission inventory.[3] To date, there is still no inorganic acid emission factor of IC-related process reported. In Taiwan, the "Handbook for Estimation of Taiwan Air Pollutant Emission" issued by TEPA in 2000 can be consulted to calculate the amount of emissions of various pollutants produced by different industries, but the emission factor for the IC manufacturing industry has not been reported yet.[4]

The objective of this study is to estimate the emission factor of inorganic acids for semiconductor manufacturing

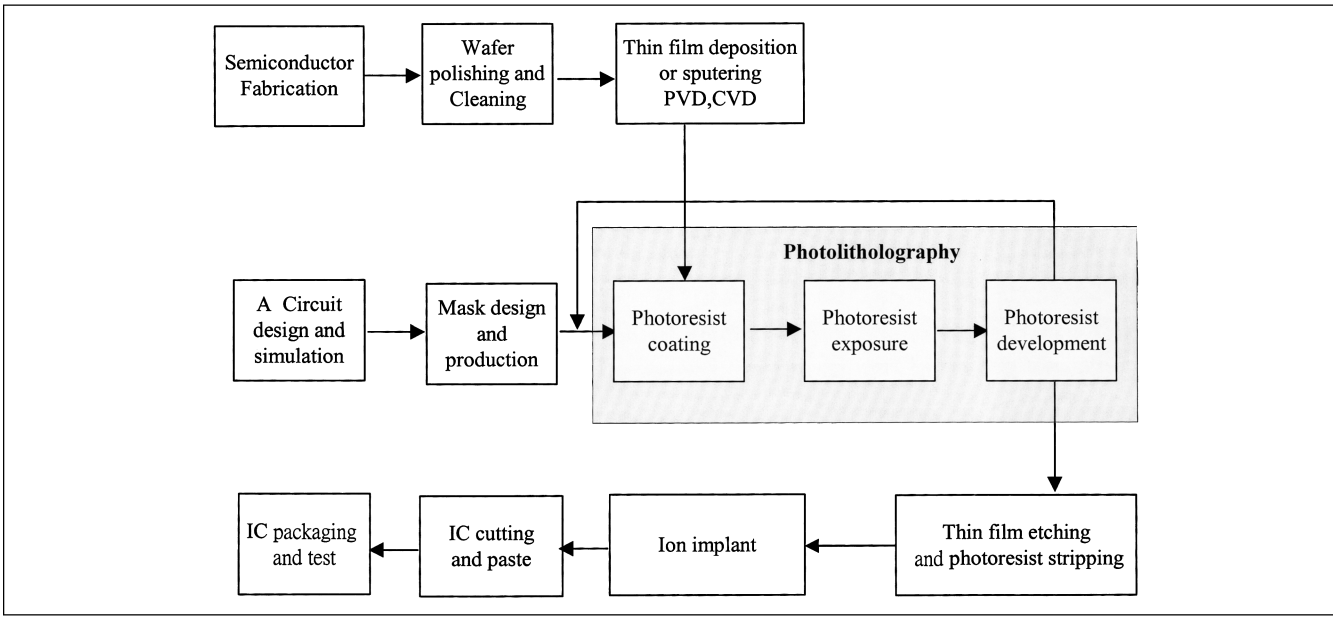

Figure 1. IC process flow diagram.

processes. This can be a reference for various governmental organizations in regulating emission control laws and policies on pollution reduction and, thus, can achieve the goal of air quality management and improvement.

Table 1. Commonly used chemicals in semiconductor processes.

Process	Method	Commonly Used Chemicals
Cleaning	—-	H_2SO_4, HCl, ammonium hydroxide (NH_4OH), hydrogen peroxide (H_2O_2), HNO_3, HF, water (H_2O), IPA, methanol, acetone, 1,1,1-trichloroethane, hexafluoroethane (C_2F_6), nitrogen trifluoride (NF_3)
Photolithography	Positive	Ortho-diazoketone, sodium hydroxide (NaOH), potassium hydroxide (KOH), polymethacrylate, polyfluoroalkyl-methacrylate, ethylene glycol, IPA, ethanolamine
	Negative	Isoprene, ethyl acrylate, xylene, n-butyl acetate, IPA
Etching	Wet	H_2SO_4, H_2O_2, phosphoric acid (H_3PO_4), HNO_3, HF, HCl
	Dry	Chlorine (Cl_2), hydrobromic acid (HBr), carbon tetrafluoride (CF_4), sulfur hexafluoride (SF_6), trifluoromethane (CHF_3), fluorine (F_2), carbon tetrachloride (CCl_4), hydrogen (H_2), boron chloride (BCl_3), freons
Oxidation	—	Trichloroethane, trichloroethylene
Deposition	—	SiH_4, $SiCl_4$, NH_3, N_2O, WF_6, AsH_3, PH_3, B_2H_6
Ion implantation and diffusion	—	AsH_3, PH_3, PF_5, BF_3, B_2H_6

METHODS

Semiconductor Fabrication

In IC fabrication, inorganic acid emission is produced mainly during the procedure of wafer surface cleaning and etching. A typical process flow of wafer fabrication is shown in Figure 1, and a list of chemicals commonly used in semiconductor process is shown in Table 1. The major air pollutants emitted from IC industries include the VOCs, such as isopropyl alcohol (IPA), acetone, propylene glycol monomethyl ether acetate (PGMEA), and ethyl acetate, and the inorganic acids, such as hydrofluoric acid (HF), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl). The emitted waste gas also includes some other toxic pollutants, such as arsenical compounds. Semiconductor fabricators (fabs) use the wet-scrubber technique (scrubbing liquid: water; pH: 8.5–9.5; circulating water flow rate: 40–55 t/hr; blow-down period: 8–24 hr) to control the inorganic gas emissions.

Table 2. "Air Pollution Regulation and Emission Standard for IC Manufacturing Industry" criterion application.[1]

Original Material	Usage Yearly (equal to or more than) kg/yr
VOCs	1700
Trichloroethylene	60
HNO_3	1700
H_2SO_4	300
HCl	1700
H_3PO_4	1700
HF	1200

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

Table 3. Production and chemical usage data of all 36 factories.

Factory	Product (unit)	Monthly Average of Product	Monthly Usage of H_2SO_4 (L/month)	Monthly Usage of HCl (L/month)	Monthly Usage of HF (L/month)
Wafer process					
Hy[a]	Si wafer-6″ (piece)	2315	133.3	58	0
Hb[a]	Si wafer-5″ (piece)	15,307	24,404.1	667.5	0
T1[a]	Si wafer-6″ (piece)	23,611	2999.5	1105.3	0
Sd	GaAS wafer (piece)	300	16,818.8	1238.1	547.5
Bd	GaAS wafer (piece)	663	0	240.1	0
It	Si wafer-8″ (piece)	1796	951.8	20.3	741.8
Ul	Si wafer-8″ (piece)	2168	0	12.1	495.9
Fb	Si wafer-8″ (piece)	2654	—	—	—
Mg	Si wafer-8″ (piece)	4367	0	3.8	4.2
Hg	Si wafer-8″ (piece)	8888	20.3	0.3	0
Fc	Si wafer-8″ (piece)	11,700	897.2	725.8	285.8
T7	Si wafer-8″ (piece)	10,367	—	—	—
Si	Si wafer-8″ (piece)	14,611	—	—	—
Sj	Si wafer-8″ (piece)	21,890	—	—	—
T5	Si wafer-8″ (piece)	23,070	40,632.8	3485.8	9303.3
Um	Si wafer-6″ (piece)	41,277	45,497.8	2566.7	4487.8
T2	Si wafer-6″ (piece)	43,395	21,334.2	2991.5	12986.2
Km	Si wafer-8″ (piece)	46,238		667.5	1121.9
T3	Si wafer-8″ (piece)	53,636	30	4.4	19884.3
Cd	Si wafer-8″ (piece)	144,016	4635	6963.3	7080
Wire frame process					
Fs	Wire frame (strip)	161,773,400	3654.2	21849.4	0
Lv	Wire frame (strip)	69,688,582	1127.1	0	0
Kg	Wire frame (strip)	3,579,230	1949.2	132.5	0
Fs3	Wire frame (strip)	1,185,664	3953.8	1860.1	0
Sl	Wire frame (strip)	1,165,589	5233.3	8626.4	0
Tj	Wire frame (strip)	—	—	—	—
Integrated circuit and crystal growth process					
Yh	Integrated circuit and crystal growth (pellet)	10,666,666	20	1.3	6.2
Sy	Integrated circuit and crystal growth (pellet)	8,614,285	5.3	6.3	0
Ht	Integrated circuit and crystal growth (pellet)	6,924,049	118.8	6732	0
Gy	Integrated circuit and crystal growth (pellet)	27,190	49.7	214	0
Hl	Integrated circuit and crystal growth (pellet)	8867	0	0	0
Kl	Integrated circuit and crystal growth (pellet)	1330	4781.5	2243.9	0
Lw	Integrated circuit and crystal growth (pellet)	1293	63.3	71.1	0
Js	Integrated circuit and crystal growth (pellet)	88	6.9	17.8	0
Other process					
Kj	Photo-mask (piece)	6390	1422.7	0	0
Sy	Wafer polish	—	1999.7	15,691	0

Note: — = Data not available; [a]These three factories had closed or moved.

Article 3 of the APRESS states that the regulation is applied to those semiconductor fabs having yearly consumption of chemicals equal to or more than the amount shown in Table 2. For the inorganic acids (i.e., HF, nitric acid [HNO_3], and HCl), the removal efficiency of operating control devices should be more than 95%, or the total emission amount of each chemical in a fab should be less than 0.6 kg/hr, whereas H_2SO_4 removal efficiency of operating control devices should be more than 95%, or the total H_2SO_4 emission amount in a fab should be less than 0.1 kg/hr. It also is mentioned in APRESS that the factories that fall under these regulation criteria should submit a seasonal report to the local environmental authority (Environmental Protection Bureau). The content of the report should include the chemical usage data, operating gas flow rate, circulating liquid flow rate, and pH value of inorganic acid control devices (wet scrubbers).

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

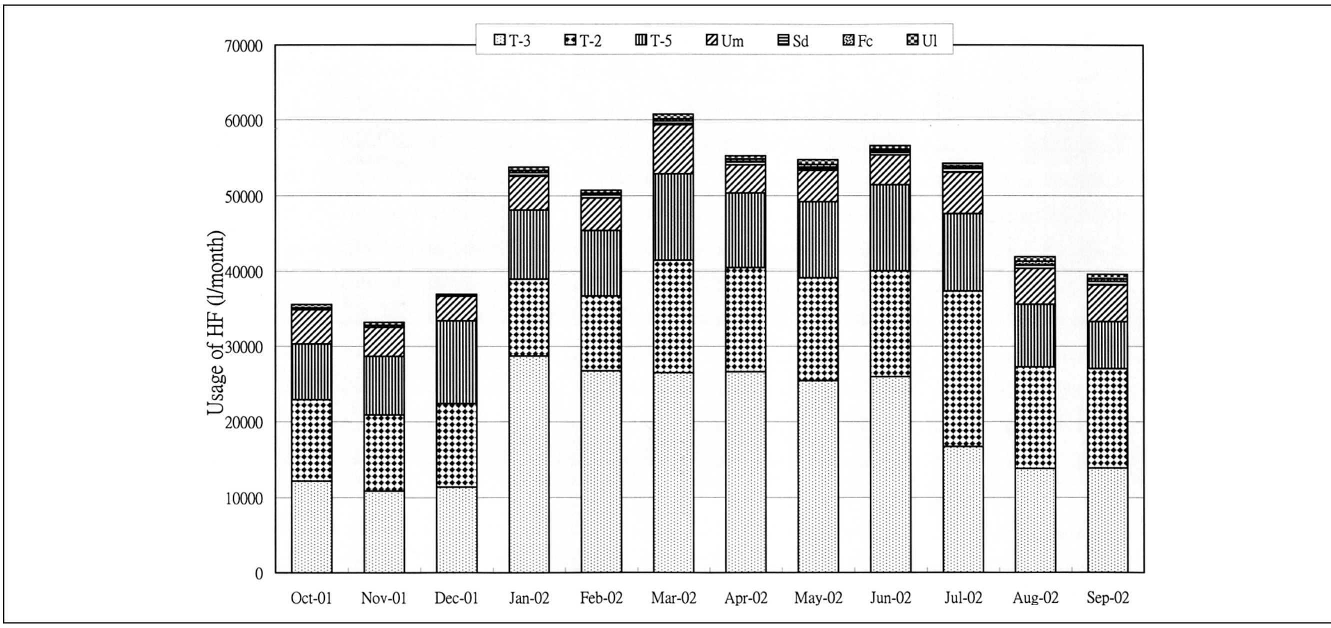

Figure 2. Monthly variation in usage amount of HF (Oct 2001–Sep 2002).

There are 36 semiconductor factories that fall under the regulation of APRESS, operating at Science-Based Industrial Park (SBIP), Hsin-chu County, Taiwan. Five to 10 fabs were selected to estimate the emission factors of HF, H_2SO_4, and HCl in this study, based on whether they use these chemicals. These fabs are better representative of the database of inorganic acid emission factors, because they are large-scale factories and involve similar types of manufacturing processes and facilities (Table 3). All of the data from some small factories are not available, but from the available data, it can be predicted that the selected fabs are the representative of the 36 factories. The collected information of representative factories includes the type and amount of chemicals used, operating flow rate, and monthly production quantity for each factory.

Emission Estimation

There is no continuous emission monitor (CEM) system for the monitoring of inorganic acid concentration. However, there are monitoring data for operating gas flow rate, circulating liquid flow rate, and pH value of wet scrubbers. For estimation of the emission of inorganic acids, the source test method was adopted. Sampling of inorganic acid was based on porous metal denuders containing a

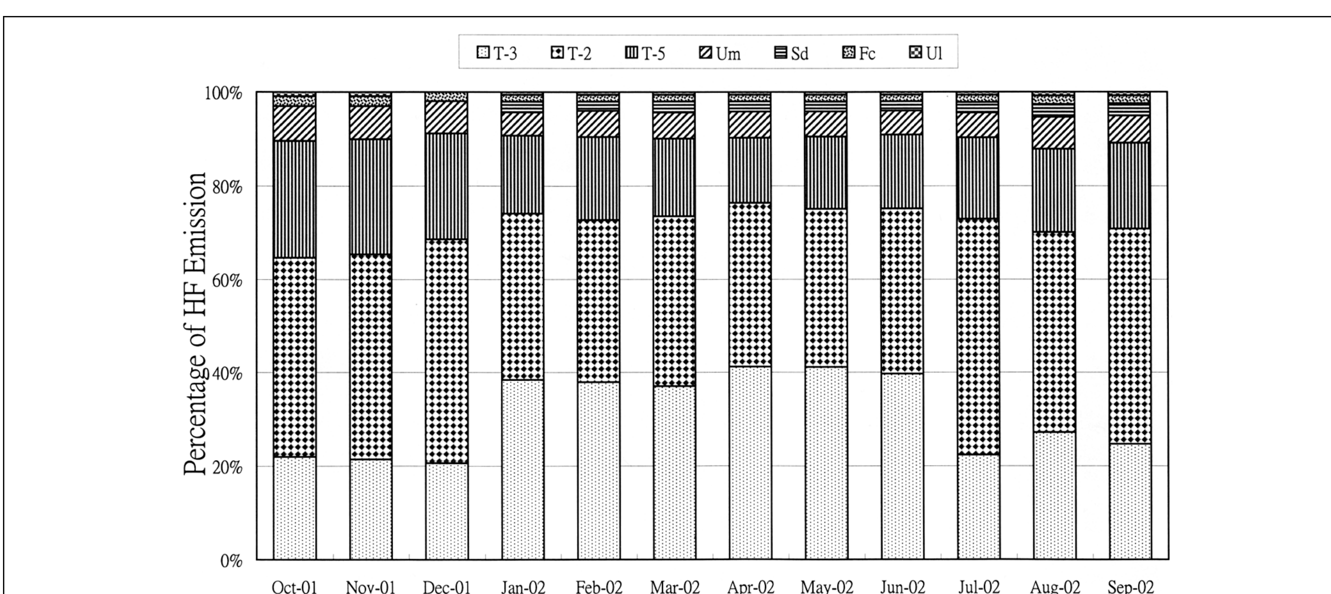

Figure 3. Monthly variation in HF emission amount (Oct 2001–Sep 2002).

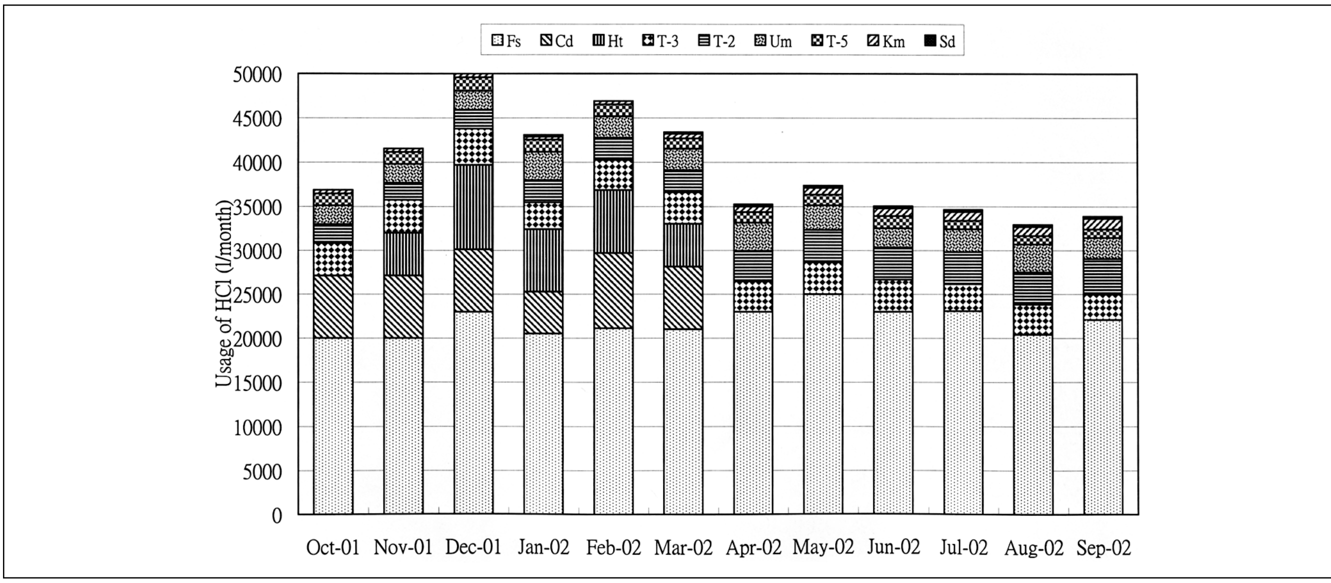

Figure 4. Monthly variation in usage amount of HCl (Oct 2001–Sep 2002).

Teflon filter to collect particles followed by two porous metal discs coated with 5% sodium carbonate (Na_2CO_3) and 4% citric acid to absorb acidic and basic gases,[5,6] respectively. The sampling flow rate was maintained at 2 L/min. After sampling, the filters were extracted with deionized water and the samples were then analyzed by ion chromatography (model 4500i, Dionex Corp.). The method used to calculate the emission amount is as follows:

$$\begin{aligned}&\text{Emission amount hourly (kg/month)}\\&= \text{actual mass concentration (g/Nm}^3) \times 10^{-3}\ \text{kg/g}\\&\times \text{average emission gas flow rate (Nm}^3\text{/hr)}\\&\times 24\ \text{(hr)} \times \text{monthly working days}\end{aligned} \quad (1)$$

Emission Factor

The emission factor is defined as the average emission of air pollutant produced by per-unit production or original chemical consumption. In this study, the emission factor (E_f) is determined by the following equation:

$$E_f = M_E/P \quad (2)$$

where M_E is pollutant mass emission per unit period (e.g., kg/day); and P is usage amount of chemicals per unit period (e.g., L/day).

The estimating steps of the emission factor[7–12] were

- Step 1: Collecting the monthly amount of chemicals used.

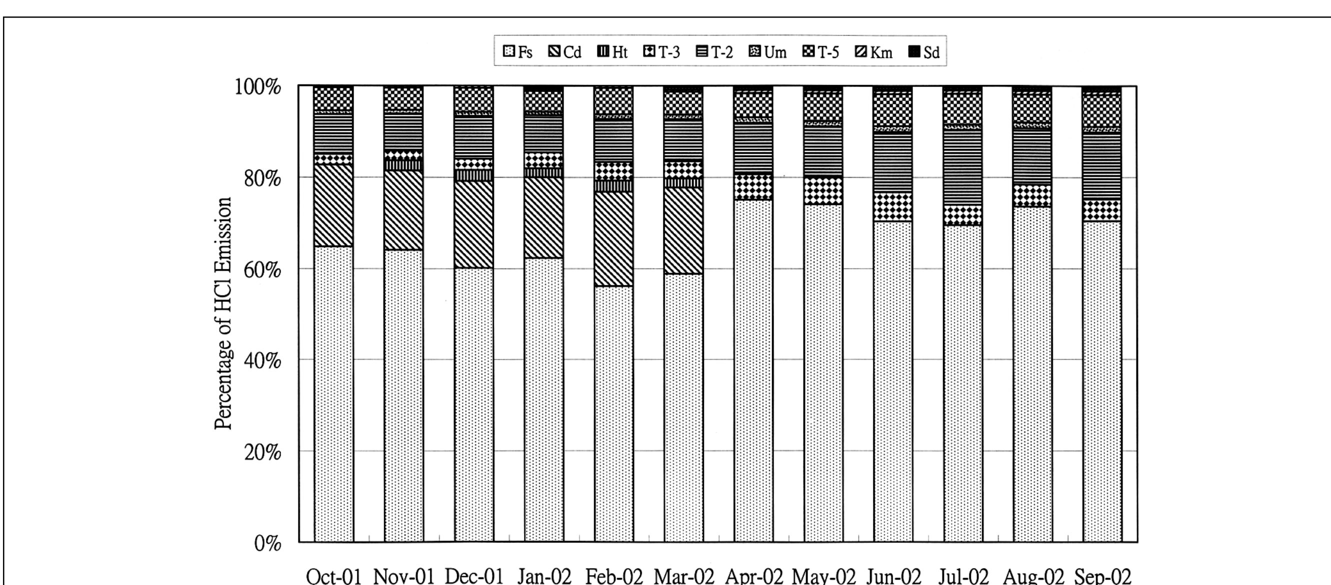

Figure 5. Monthly variation in HCl emission amount (Oct 2001–Sep 2002).

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

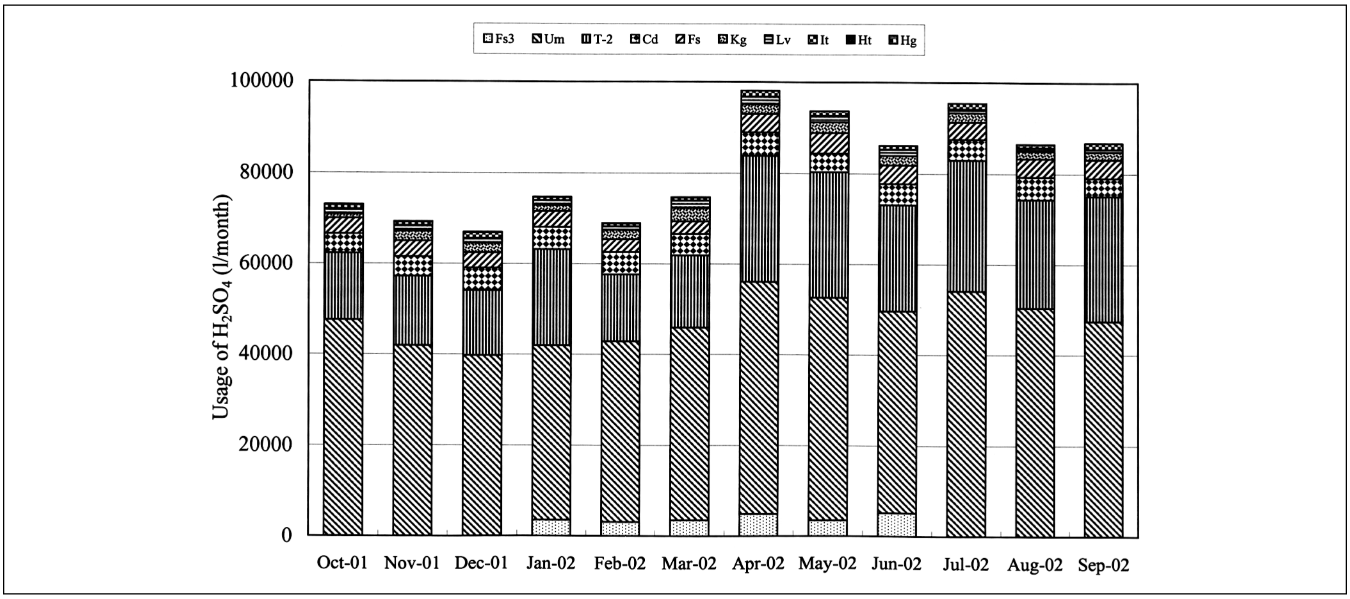

Figure 6. Monthly variation in usage amount of H_2SO_4 20 (Oct 2001–Sep 2002).

- Step 2: Analyzing the relationship between the total amount of chemicals used and the original emission amount per unit period for selected fabs.
- Step 3: Estimating the emission factor for each semiconductor factory. The calculation was based on the amount of pollutant emitted per unit usage amount of chemicals.
- Step 4: A linear regression function ($y = ax$) was employed to fit the data of usage amount of chemicals and emission amount from different fabs. The correlation coefficient (R^2) also was determined to verify the relationship, and the emission factor was presented.

Emission Characteristic

Inorganic acid emission profiles of six typical IC manufacturing fabs (i.e., T-2, T-3, T-5, Um, Cd, and Sd fabs) were determined by carrying out the stack sampling using the porous method denuders sampler. The samples were analyzed by ion chromatography.

RESULTS

Figure 2 shows the monthwise total usage of HF for each factory. The monthly variation in the HF emission amount is represented in Figure 3. Figures 4 and 5 show the monthly total usage and emission of HCl for each factory, respectively. The monthly variation in H_2SO_4 total usage and emission amount are represented in

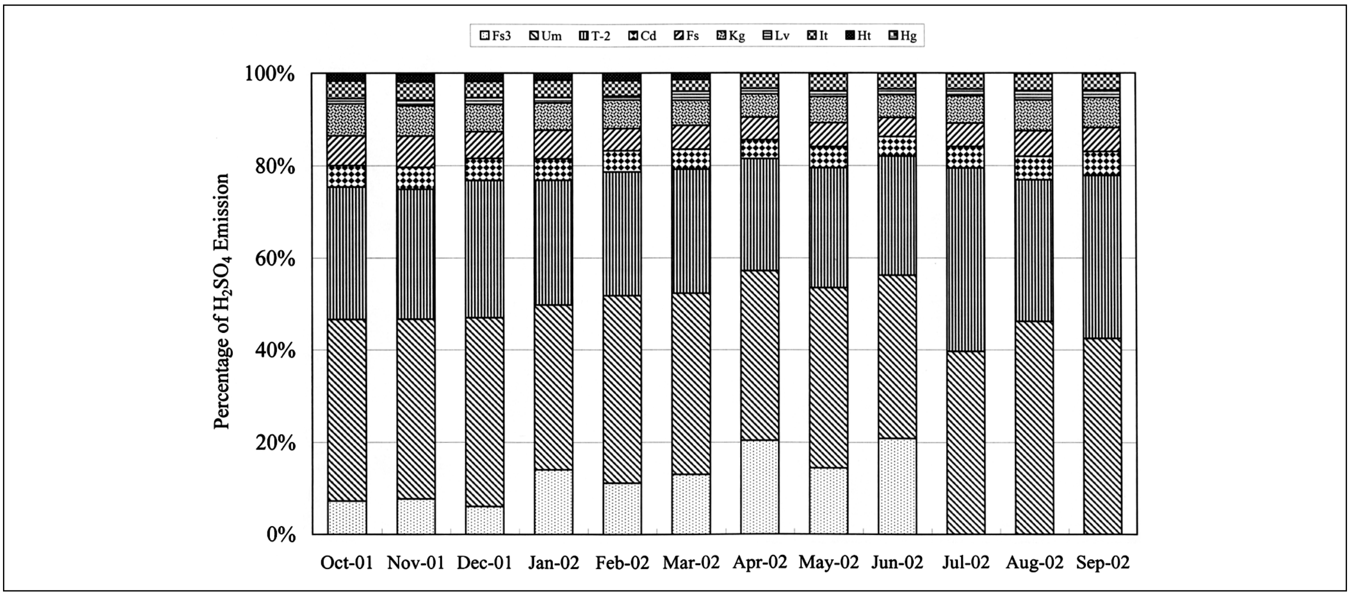

Figure 7. Monthly variation in H_2SO_4 emission amount (Oct 2001–Sep 2002).

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

Table 4. Monthly average emission factor of HF (kg/L).

Fab	Oct 01	Nov 01	Dec 01	Jan 02	Feb 02	Mar 02	Apr 02	May 02	Jun 02	Jul 02	Aug 02	Sep 02	Avg.	CV (%)
T-3	0.004	0.004	0.004	0.004	0.004	0.004	0.005	0.005	0.005	0.004	0.005	0.004	0.0043	11.4
T-2	0.008	0.009	0.010	0.010	0.010	0.007	0.007	0.008	0.008	0.007	0.008	0.009	0.0084	13.8
T-5	0.007	0.006	0.005	0.005	0.006	0.004	0.004	0.005	0.004	0.005	0.005	0.007	0.0053	20.1
Um	0.003	0.004	0.005	0.003	0.004	0.003	0.004	0.004	0.004	0.003	0.003	0.003	0.0039	18.7
Sd	—	—	—	0.014	0.014	0.014	0.014	0.015	0.011	0.012	0.012	0.013	0.0132	9.8
Fc	0.017	0.016	0.017	0.016	0.017	0.015	0.014	0.013	0.018	0.017	0.010	0.013	0.0153	15.3
Ul	0.004	0.005	—	0.004	0.004	0.003	0.004	0.003	0.004	0.005	0.003	0.003	0.0038	19.7
Average 0.0075 (CV = 60.7%, n = 80)														

Notes: — = Data not available; CV = Coefficient of variation; n = Number of data.

Table 5. Monthly average emission factor of HCl (kg/L).

Fab	Oct 01	Nov 01	Dec 01	Jan 02	Feb 02	Mar 02	Apr 02	May 02	Jun 02	Jul 02	Aug 02	Sep 02	Avg.	CV (%)
Fs	0.015	0.015	0.012	0.015	0.010	0.013	0.012	0.011	0.010	0.010	0.012	0.010	0.0121	16.7
Cd	0.012	0.011	0.012	0.019	0.010	0.012	—	—	—	—	—	—	0.0127	25.3
T-2	0.019	0.020	0.019	0.016	0.015	0.017	0.011	0.011	0.011	0.015	0.011	0.011	0.0147	24.4
T-5	0.018	0.017	0.015	0.017	0.017	0.020	0.016	0.018	0.016	0.024	0.021	0.022	0.0184	14.9
T-3	0.0029	0.0027	0.0027	0.0058	0.0046	0.0049	0.0057	0.0057	0.0055	0.0050	0.0045	0.0050	0.0046	25.6
Um	0.0018	0.0017	0.0019	0.0012	0.0016	0.0018	0.0013	0.0015	0.0018	0.0015	0.0013	0.0015	0.0016	14.6
Ht	—	0.0021	0.0011	0.0014	0.0013	0.0019	—	—	—	—	—	—	0.0016	27.0
Km	0.0049	0.0054	0.0054	0.0056	0.0052	0.0044	0.0037	0.0031	0.0027	0.0024	0.0024	0.0019	0.0039	35.2
Sd	—	—	—	0.019	—	0.020	0.014	0.014	0.014	0.014	0.015	0.014	0.0155	16.2
Average 0.0096 (CV = 68.2%, n = 91)														

Notes: — = Data not available; CV = Coefficient of variation; n = Number of data.

Table 6. Monthly average emission factor of H_2SO_4 (kg/L).

Fab	Oct 01	Nov 01	Dec 01	Jan 02	Feb 02	Mar 02	Apr 02	May 02	Jun 02	Jul 02	Aug 02	Sep 02	Avg.	CV (%)
Um	0.00041	0.00043	0.00049	0.00049	0.00049	0.00052	0.00041	0.00042	0.00045	0.00036	0.00041	0.00038	0.00044	11.3
T-2	0.00096	0.00086	0.001	0.00067	0.00087	0.00094	0.00050	0.0005	0.00062	0.00067	0.00057	0.00055	0.00073	25.9
Fs3	—	—	—	0.0021	0.0017	0.0021	0.0024	0.0022	0.0023	—	—	—	0.00213	11.4
Kg	0.0038	0.0014	0.0013	0.0023	0.0014	0.001	0.0013	0.0013	0.0013	0.0014	0.0018	0.0016	0.00166	45.2
Fs	0.00091	0.00089	0.00081	0.00094	0.00081	0.001	0.00068	0.00061	0.00057	0.00066	0.00061	0.00055	0.00075	21
Cd	0.00054	0.00051	0.00046	0.00049	0.00044	0.00050	0.00045	0.00059	0.00050	0.00049	0.00045	0.00055	0.0005	9.11
It	0.0021	0.0024	0.0014	0.0029	0.0024	0.0023	0.0014	0.002	0.0021	0.0013	0.0021	0.0011	0.00196	27.8
Ht	0.0064	0.0067	0.0065	0.0063	0.0064	0.0065	—	—	—	—	—	—	0.00647	2.1
Lv	0.00050	0.00046	0.00064	0.00061	0.00055	0.00065	0.00043	0.00048	0.00054	0.00087	0.00126	0.00106	0.00067	38.7
Hg	0.0032	0.0045	0.0037	0.0039	0.0033	0.0041	—	0.0047	0.0045	0.0046	0.0044	0.0033	0.00402	14.2
Average 0.0016 (CV = 99.2%, n = 107)														

Notes: — = Data not available; CV = Coefficient of variation; n = Number of data.

Figures 6 and 7, respectively. The data of HF, HCl, and H_2SO_4 emission factors, E_f, are given in Tables 4, 5, and 6, respectively.

According to Table 4, the final average value of the emission factor (i.e., E_f for HF) is estimated to be 0.0075 kg/L (coefficient of variation [CV] = 60.7%, n = 80). To justify the relationship between the amount of usage of HF (see Figure 2) and the HF emission amount (see Figure 3), a linear regression statistics analysis (for n = 80) was performed as shown in Figure 8. The linear regression equation is determined to be $y = 0.0052x$ (where y = HF emission amount, x = usage amount of HF). The regression analysis shows that E_f is equal to 0.0052 kg/L with correlation coefficient (R^2) = 0.82, which is close to the estimated emission factor.

According to Tables 5 and 6, the final average values of E_f for HCl and H_2SO_4 are estimated to be 0.0096 kg/L (CV = 68.2%, n = 91) and 0.0016 kg/L (CV = 99.2%, n = 107), respectively. To justify the relationship between the usage amount of HCl and H_2SO_4 (see Figures 4 and 6) and their emission amount (see Figures 5 and 7), the linear regression statistics analysis were performed as shown in Figures 9 and 10, respectively. The linear regression equations are determined to be $y = 0.011x$ for HCl (n = 91) and $y = 0.00048x$ for H_2SO_4 (n = 107). The emission factors determined by regression analysis (i.e., E_f for HCl) is equal to 0.011 kg/L with R^2 = 0.9, which is almost the same as the estimated value, whereas for H_2SO_4, E_f is equal to 0.00048 kg/L with R^2 = 0.84. The difference between estimated and regression analysis values of E_f for H_2SO_4 attributed as the CV of the estimated value is very high, which may be because of the comparatively lower E_f (because of the low emission rates and high usage of H_2SO_4).

To understand the emission characteristics, inorganic acid emission profiles of eight typical IC manufacturing fabs were determined by ion chromatography analysis. Figures 11 and 12 show the gas and the particle emission profiles of inorganic acids for T-2, T-3, T-5, Um, Cd, and Sd fabs.

DISCUSSION

In general, the monthly usage of chemicals in all the factories is found to be consistent. Figures 2, 4, and 6 show the variation profiles of total usage of HF, HCl, and H_2SO_4, respectively, and are mostly steady except for the variation in factory T-3 in Figure 2. Similarly, Figures 3, 5, and 7 show that the monthly variation in the emission amounts of all the factories is very stable except for factory T-3 in Figure 3. This also can be seen in Figures 8–10 (i.e., the R^2 values show that the usage amount of chemicals and the emission amount are correlated quite considerably). In other words, while the amount of chemical usage increases, the emission amount also increases proportionally.

The emission factors of HF, HCl, and H_2SO_4 for the wafer production processes of the IC industries are estimated to be 0.0075, 0.0096, and 0.0016 kg/L, respectively. According to Figure 11, the most dominant gas emission in factories T-2, T-3, T-5, Um, and Sd is HF, which is emitted mainly from the cleaning and etching processes. For example, in the emission profile of factory T-2, the dominant chemicals are HF (85%) and HCl (15%). In addition, HNO_3 is present in the emission profiles of

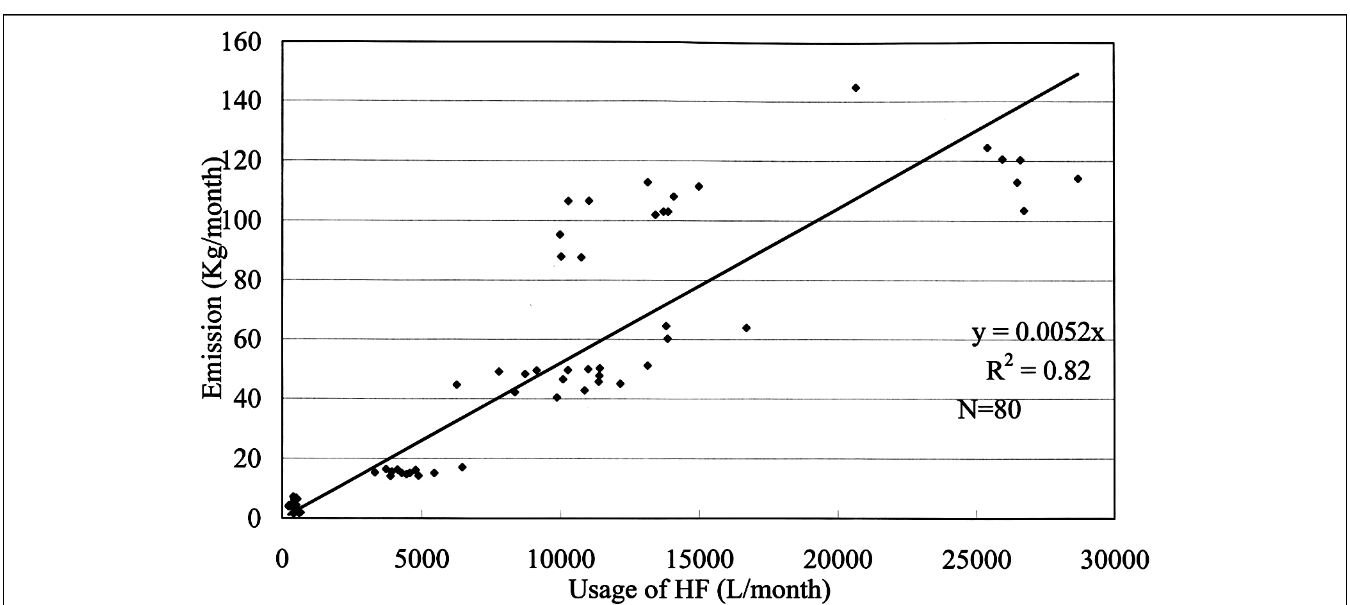

Figure 8. Relationship between emission and usage of HF in semiconductor manufacturing processes.

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

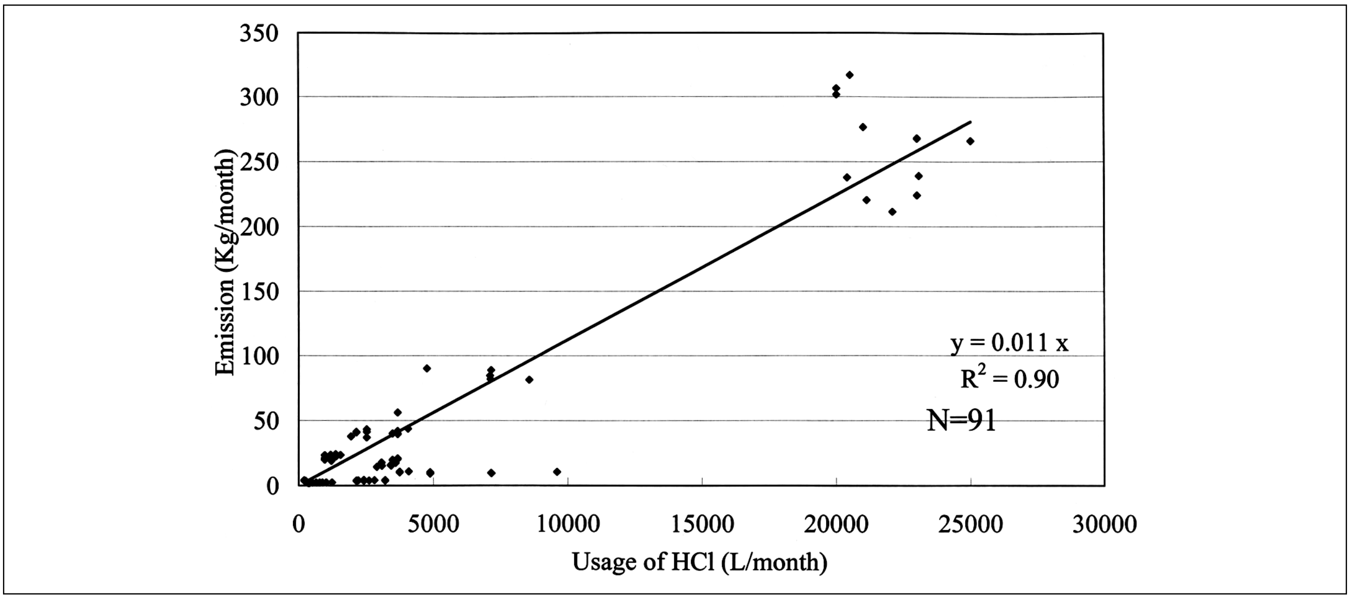

Figure 9. Relationship between emission and usage of HCl in semiconductor manufacturing processes.

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

factory Cd, while it is totally absent in factories T-2, T-3, T-5, Um, and Sd profiles, depending on what kind of chemicals the fabs are using. A significant amount of HNO_3 emissions (74%) is identified in factory Cd.

Figure 12 shows the particle emission profiles of inorganic acids. Based on this figure, the most dominant species of the emission is fluorine (F^-) in factories T-5 and Sd. However, in factories T-2 and T-3, the H_2SO_4 droplet is the main component of the emissions. In the Sd emission profile, chlorine (Cl^-) is the most dominant emission species. A significant amount of nitrate (NO_3^-) emission is identified in factories Cd and T-3 profiles, but they are totally absent in factory T-2 and Sd profiles. In summary, the six emission profiles of fabs T-2, T-3, T-5, Um, Cd, and Sd can be treated as the representative profiles for the fabs considered in this study.

CONCLUSIONS

Emission factors are estimated to be 0.0075 kg/L with CV = 60.7%, n = 80 (HF); 0.0096 kg/L with CV = 68.2%, n = 91 (HCl); and 0.0016 kg/L with CV = 99.2%, n = 107 (H_2SO_4) for semiconductor manufacturing processes based on the collected data and analyzed from typical fabs. Care should be taken to apply these emission factors

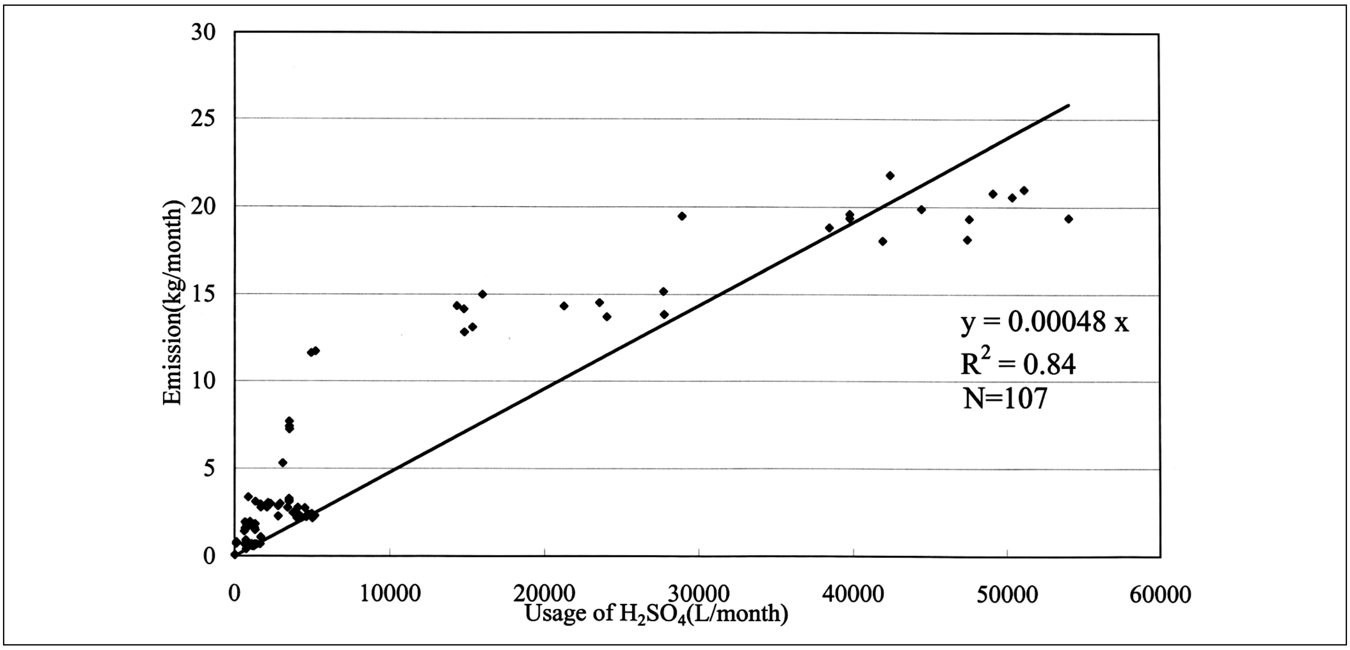

Figure 10. Relationship between emission and usage of H_2SO_4 in semiconductor manufacturing processes.

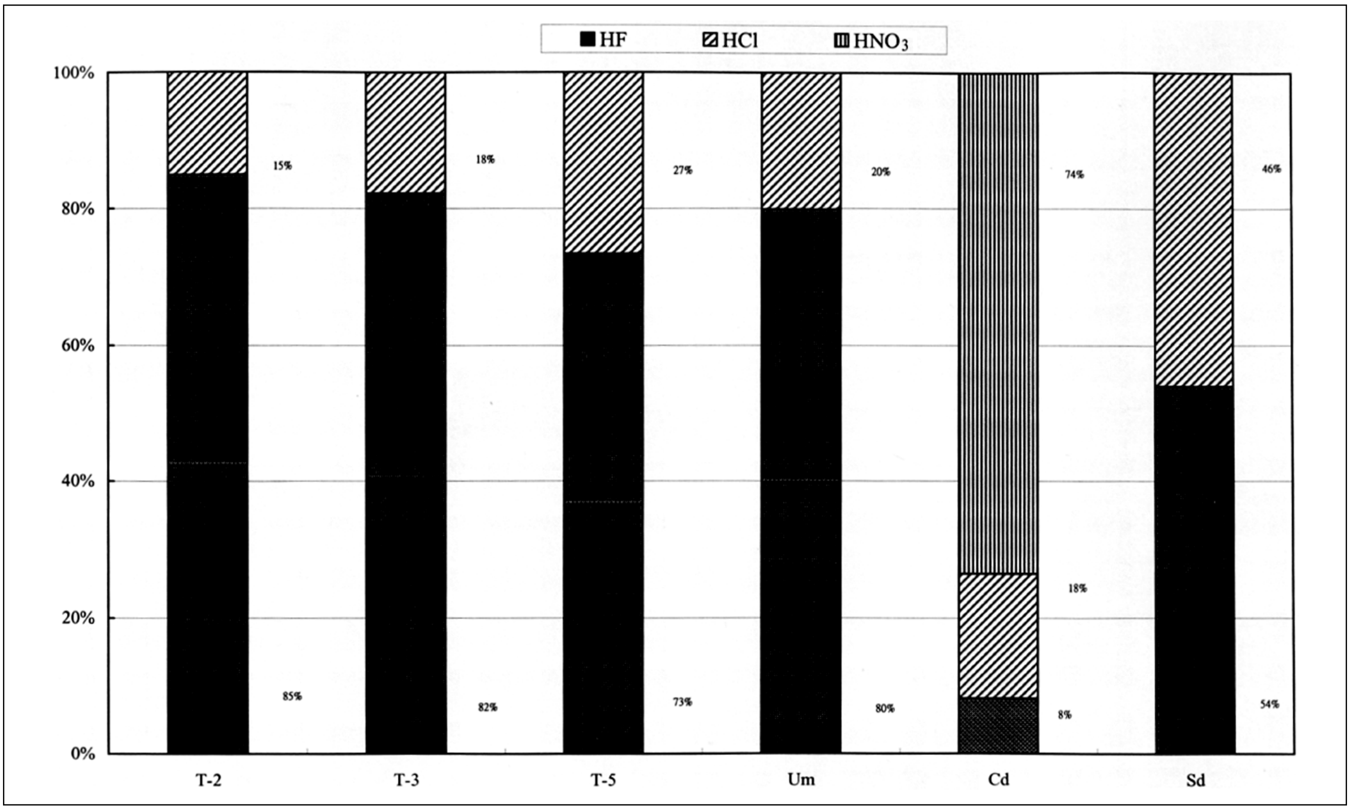

Figure 11. Gas inorganic acid emission profiles of six semiconductor manufacturing fabs.

in many situations, such as in ambient dispersion modeling and analysis, control strategy development, and screening sources for compliance investigation. These emission factors represent the average value from limited fab source data without consideration of control equipment. Average emissions may differ significantly from source to source as shown by the CV in this study (see Tables 4–6). The emission would be greatly reduced if control equipment was properly selected, installed, and operated. In addition, the emission profiles represent the fingerprint of the fab emission and show that HF is the most dominant chemical in the gaseous emission of al-

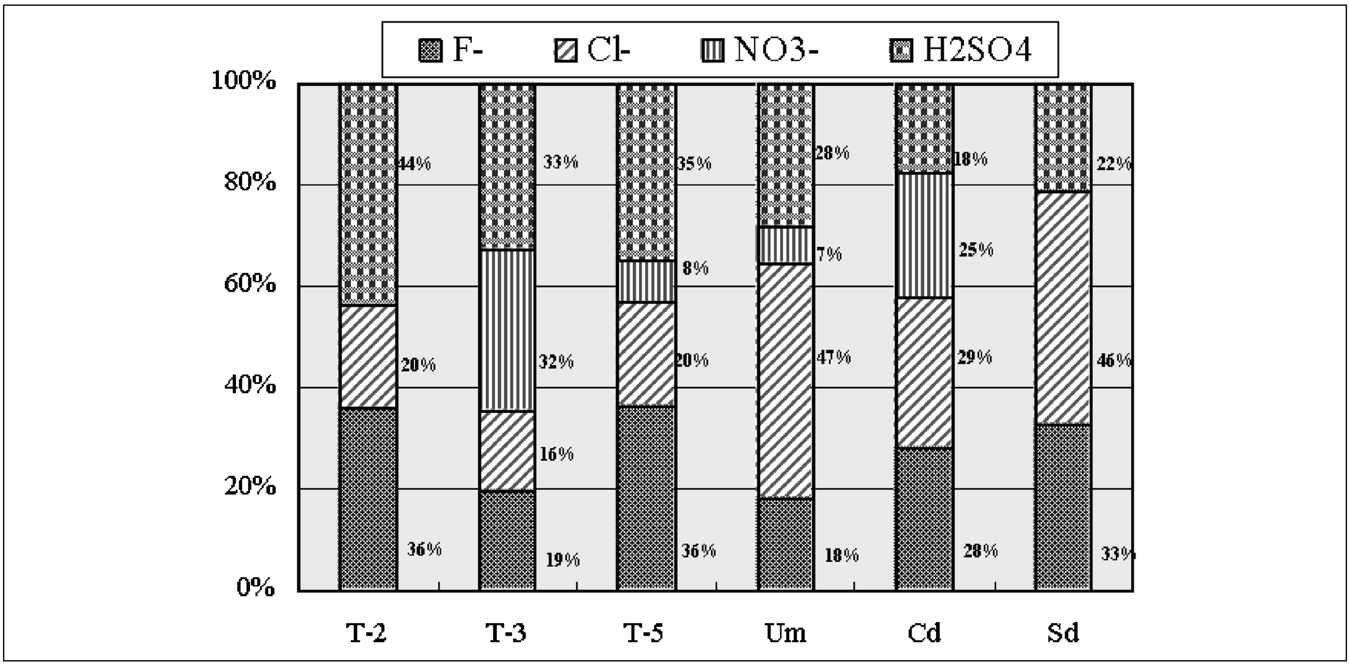

Figure 12. Particle inorganic acid emission profiles of six semiconductor manufacturing fabs.

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014

most all fabs; however, in the fingerprint of particle emission, the H_2SO_4 droplet, F^-, and Cl^- are the main emission species, which depends on whether the fab is using the chemical.

REFERENCES

1. *Air Pollution Regulation and Emission Standard for Semiconductor Manufacturing Industry*; Taiwan Environmental Protection Administration: Taipei, Taiwan, Republic of China, April 2000.
2. *Compilation of Air Pollutant Emission Factor Volume I: Stationary Point and Area Sources,* 5th ed.; U.S. Environmental Protection Agency: Raleigh, NC, January 1995.
3. *The Emission Inventory: Regional Strategies for the Future, Proceedings of a Specialty Conference*; Air & Waste Management Association and U.S. Environmental Protection Agency: Raleigh, NC, October 1999.
4. *Handbook for Estimation of Taiwan Air Pollutant Emission*; Environmental Protection Administration: Taipei, Taiwan, Republic of China, September 2000.
5. Tsai, C.J.; Huang, C.H.; Wang, S.H.; Shin, T.S. Design and Testing of a Personal Porous-Metal Denuder; *Aerosol Sci. Technol.* **2000**, *35*, 611-616.
6. Tsai, C.J.; Perng, S.B.; Chiou, S.F. Use of Two Different Acidic Aerosol Samplers to Measure Acidic Aerosols in Hsinchu, Taiwan; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 2120-2128.
7. Chein, H.M.; Chen, T.M. Estimation of VOCs Emission Factor for Semiconductor Manufacturing Processes. In *Proceedings of Air Pollution IX*, Wessex Institute of Technology, United Kingdom, September 2001; pp 491-500.
8. Chein, H.M.; Chen, T.M. Study in the Estimation of VOCs Emission Factor for Semiconductor Manufacturing. In *Proceedings of the 18th Air Pollution Control Technology Conference*, Taiwan, Republic of China, 2000; p 2–8.
9. Chein, H.M.; Chen, T.M. Emission Characteristics of Volatile Organic Compounds from Semiconductor Manufacturing; *J. Air & Waste Manage. Assoc.* **2003**, *53*, 1029-1036.
10. Chein, H.M.; Chen, T.M. *Air Quality Improvement Project in Hsinchu Industry Park*; Industrial Technology Research Institute: Hsin-chu, Taiwan, Republic of China, 2000.
11. Chein, H.M.; Chen, T.M. *Auditing and Control Project of Air Quality High Technology Industry in Hsinchu Science Industry Parks*; Industrial Technology Research Institute: Hsin-chu, Taiwan, Republic of China, 2002.
12. Chein, H.M.; Chen, T.M. *Auditing and Control Project of Air Quality for Science and Technology Industry in Hsinchu Science Industry Parks*; Environmental Protection Bureau: Hsin-chu, Taiwan, Republic of China, 2002.

About the Authors

Dr. HungMin Chein is a researcher and deputy division director, Tzu Ming Chen is an associate researcher, and Dr. Shankar Gopala Aggarwal is a researcher in the Environmental Health and Air Pollution Division, Center for Environmental, Safety, and Health Technology Development, Industrial Technology Research Institute, Hsin-chu, Taiwan. Dr. Chuen-Jinn Tsai is a professor and Chun-Chao Huang is a graduate student in the Institute of Environmental Engineering, National Chiao Tung University, Hsin-chu, Taiwan. Address correspondence to: HungMin Chein, Building 32, No. 195, Section 4, Chung Hsing Road, Chutung, Hsin-chu, 310 Taiwan; fax: 886-3-5918753; e-mail: hmchein@itri.org.tw.

Downloaded by [National Chiao Tung University] at 01:27 30 April 2014