Guest Forum

Airborne Molecular Contamination Control Technology in the Semiconductor Industry

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Dan-Takuma Technologies Inc. will begin to sell a continuous trace analyzer for monitoring Airborne Molecular Contamination (AMC). This DT Analyzer will be produced for the semiconductor industry as a part of the AMC control technology under contract with the HORIBA Group. This paper is an outline of AMC control technology including AMC measurement in the air inside a clean room.

Introduction

Moore's Law, predicted by Dr. Gordon Moore in 1965, states that the number of components on chips with the smallest manufacturing costs per component doubles roughly every 18 to 24 months, and is widely used as a guideline in the semiconductor industry even now, 40 years later. Moore's Law has been supported by many peripheral technologies such as ultrafine lithography. As lithography produces smaller and smaller lines for integrated circuits, the equipments and environment of the clean room have changed largely. Conventional methods of removing contaminants in a clean room was mainly measures for particles, but presently those where also airborne molecular contaminants are controlled have become standard.

In particular once the technology node[*1] went below 250 nm the removal of Airborne Molecular Contamination(AMC) was adopted as part of production. Since then, as miniaturization progresses further and further, with sizes as small as 180 nm, 130 nm, 90 nm, and 65 nm, AMC control has become an increasingly important subject.
Dan-Takuma Technologies Inc. has already introduced "Executing Environmental Analysis" and "Manufacturing and selling of the chemical filter for removal of AMC" as AMC control measures for these industries. Dan-Takuma Technologies Inc. has begun sales of the continuous monitor (DT analyzer) for AMC monitoring in cooperation with HORIBA Ltd. and HORIBA Advanced Techno Co. Ltd.
This paper gives a general overview of AMC control technology.

*1: Half of the minimum distance between wires of the DRAM (DRAM half pitch).

AMC Control Technology in the Semiconductor Manufacturing Industries

AMC in the Air of a Clean Room

The main sources of AMC in the air of a clean room are outside air, personnel, the structures that make up the room, and devices and chemicals used in the room itself. These AMC are classified in SEMI[*2] and SEMATECH[*3], as shown in Table 1, into Acids, Bases, Condensable organic compounds, and Dopants. The following classifications (A, B, C and D) are simplified groups that are often used when discussing AMC.

Table 1 Classification of AMC

Acids (A)	Corrosive electron acceptor
Bases (B)	Corrosive electron donor
Condensable organic compounds (C)	Substances which have boiling points higher than room temperature under atmospheric pressure and which could potentially condense on the clean surfaces of wafers etc.
Dopants (D)	Chemical elements that form electrical characteristics of semiconductor materials.

JACA (Japan Air Cleaning Association) uses the same classification in its report "Classification of Air Cleanliness for Airborne Molecular Contamination Level in clean rooms and Associated Controlled Environments and Its Measurement Methods" in JACA No. 35 A-2003. This report shows the typical environmental concentration of a clean room. Some of the data are extracted in Table 2. In addition to contaminants A, B, C and D the table also includes "Metals" and "Organic compounds with low boiling points."

Table 2 Environmental Concentration of AMC[1]

Group	Substance or sub-group name	Concentration $10^{-N}g/m^{3*}$
Acids	HF	9, 8, 7, 6, **5, 4, 3, 2**
	HCl	9, 8, 7, 6, **5, 4, 3, 2**
	Cl_2	9, 8, 7, 6, **5, 4, 3, 2**
	HBr	9, 8, 7, 6, **5, 4, 3, 2**
	NO	9, 8, 7, 6, 5, **4, 3, 2**
	NO_2	9, 8, 7, 6, 5, **4, 3, 2**
	SO_2	9, 8, 7, 6, 5, **4, 3, 2**
	SO_3	9, 8, 7, 6, 5, **4, 3, 2**
	H_2S	9, 8, 7, 6, **5, 4, 3, 2**
Bases	NH_3	9, 8, 7, 6, 5, **4, 3, 2**
	RNH_2, R_2NH, R_3NH	9, 8, 7, 6, 5, **4, 3, 2**
	$RNH_2(OH)$	9, 8, 7, 6, 5, **4, 3, 2**
	R_4N+X-	9, 8, 7, 6, 5, **4, 3, 2**
	HMDS	9, 8, 7, 6, 5, **4, 3, 2**
Condensable organic compounds	HMDS	9, 8, 7, 6, 5, **4, 3, 2**
	TMSiOH	9, 8, 7, 6, 5, **4, 3, 2**
	BHT	9, 8, 7, 6, 5, **4, 3, 2**
	Aromatics	9, 8, 7, 6, 5, 4, **3, 2**
	Siloxane	9, 8, 7, 6, 5, 4, **3, 2**
	Phthalates	9, 8, 7, 6, 5, **4, 3, 2**
	Phosphates	9, 8, 7, 6, 5, **4, 3, 2**
	Urethanes	9, 8, 7, 6, 5, **4, 3, 2**
	THC(for GC/MS)	9, 8, 7, 6, 5, 4, **3, 2**
Dopants	BF_3, $B(OH)_3$	9, 8, 7, 6, 5, **4, 3, 2**
Metals	Na	9, 8, 7, 6, 5, **4, 3, 2**
	Mg	9, 8, 7, 6, 5, **4, 3, 2**
	Al	9, 8, 7, 6, 5, **4, 3, 2**
	K	9, 8, 7, 6, 5, **4, 3, 2**
	Ca	9, 8, 7, 6, 5, **4, 3, 2**
	Cr	9, 8, 7, 6, 5, **4, 3, 2**
	Mn	9, 8, 7, 6, 5, **4, 3, 2**
	Fe	9, 8, 7, 6, 5, **4, 3, 2**
	Cu	9, 8, 7, 6, 5, **4, 3, 2**
	Zn	9, 8, 7, 6, 5, **4, 3, 2**
Organic compounds with low boiling points	THC	9, 8, 7, 6, 5, 4, 3, **2**
	NMHC	9, 8, 7, 6, 5, 4, **3, 2**
	UHC	9, 8, 7, 6, 5, 4, **3, 2**
	HCHO	9, 8, 7, 6, 5, **4, 3, 2**

* The numerals in the table correspond to N, and the numerals without dark halftone dots indicate the typical environmental concentratrion in a clean room.

*2:SEMI (Semiconductor Equipment and Materials International): International industry body dealing with semiconductor equipment and materials.

*3:SEMATEC (Semiconductor Manufacturing Technology):A joint government and private sector body involved in research and development related to semiconductor manufacturing. Funded by the US Department of Defense and four non-governmental semiconductor manufacturers.

How to Reduce AMC

Chemical filters are generally used to reducing AMC and several chemical filters are already in commercial use. Initially chemical filters on which the chemical affixing treatment was performed by means of the neutralization method were mainly used, but recently the number of chemical filters using the ion exchange method has increased.

Dan-Takuma Technologies Inc. has, for the past 10 years (including the Takuma Co., Ltd. era), been manufacturing and selling various chemical filters (under the name PURATEX®) principally utilizing the ion exchange technology, and including the physical absorption function of high performance activated carbon. The basic technology and outline are described as follows.

Outline of the PURATEX Chemical Filter

The product with the highest market penetration rate among the PURATEX chemical filters is the CS (Cell Structure) type chemical filter, which was developed mainly for the purpose of mounting on Fan Filter Units (FFU). Compared with many other filters the CS is small, but it is characterized by having low-pressure loss and can maintain a high removal rate over a long period.

The basic structure for guarding against acids and bases is that the ion exchange resin, which is used mostly in ultra pure water manufacturing equipment, is evenly fixed on the polyurethane foam substrate, which has a three dimensional reticular framework.

For measures against condensable organic compounds, high performance activated granular carbon is evenly fixed on the same substrate.

Table 3 shows sources of AMC, corresponding chemical filters and method of removal.

Table 4 shows filter installation system[*4] and corresponding chemical filters.

*4: Filter medium.

Table 3 Classification of AMC and Corresponding Chemical Filters

	Sources	Corresponding chemical filters	Method of removal
Acids Hydrofluoric acid, Hydrochloric acid, Sulfuric acid, Nitric acid, etc.	Outside air, process Chemicals, etc.	Anion filter (A) Activated carbon filter (A)	Ion exchange Neutralization
Bases Ammonia, Amine, etc.	Outside air, personnel, concrete, paint, construction materials, process chemicals, etc.	Cation filter (C) Activated carbon filter (C)	Ion exchange Neutralization
Condensable organic substances Siloxane, Phthalate ester, Phosphate ester, etc.	Sealant, construction materials, etc.	Activated carbon filter (K)	Physical absorption
Dopant Boron, Phosphorus	HEPA, ULPA, process chemicals, etc.	Anion filter (A)	Ion exchange Complex formation reaction for Boron

Table 4 Filter Installation System and Corresponding Chemical Filters

Filter installation system		Air velocity	Type	Filter media
Outer air processing system		up to 3.0 m/s	MTO-* HS-*	Activated granular carbon Honeycomb activated carbon
			MT-**	Molding activaed carbon + Ion exchange fiber
			CS-*	Ion exchange resin Activated granular carbon
Circulation system	FFU	0.3 to 1.0 m/s	CS-*	Ion exchange resin Activated granular carbon
			PL-*	Ion exchange fiber Fiber activated carbon
	AHU	2.5 m/s	MT-CS-*	Ion exchange resin Activated granular carbon
			MC-*	Ion exchange fiber
			HS-*	Honeycomb activated carbon
Partial air supply system to Mini-en/ Loader section etc.		up to 3.0 m/s	MT-CS-*	Ion exchange resin Activated granular carbon
			HS-*	Honeycomb activated carbon
Manufacturing equipment		0.3 to 1.0 m/s	CS-*	Ion exchange resin Activated granular carbon
			PL-*	Ion exchange fiber Activated granular carbon

Replace the * with "A", "C", or "K" from Table 3 for the corresponding chemical filter.

AHU: Air Handling Unit, Mini-en: Mini Environment.

Figure 1 shows an example of a chemical filter installed in a clean room. This filter is designed for a fan filter unit (FFU). In places where the speed of air velocity is high, such as the return shaft, the tray type filter with the low air velocity of media is installed.

In order to control the gas generated from the substrate of all types, out gas is controlled by performing the aging treatment very carefully at each process.

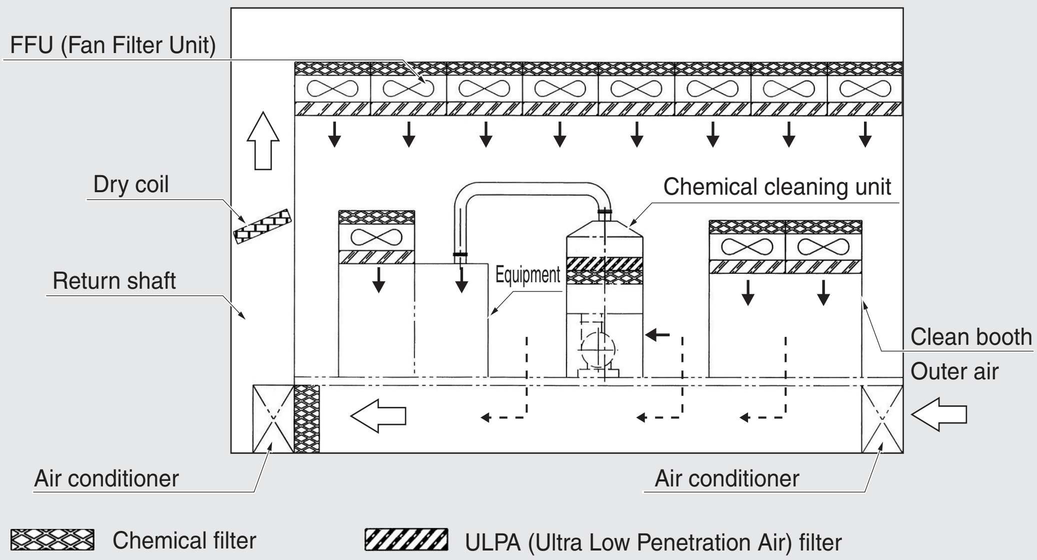

Figure 1 Example of Filter Application in a Clean Room

Ion Exchange Filter

There are two types of PURATEX chemical filter; one uses ion exchange resin, and the other uses ion exchange fiber. Both types incorporate the following ion exchange group in the substrate: the cation filter incorporated the sulfonic acid group as the strong acidic cation exchange group, and the anion filter incorporates fixed ions of the quaternary ammonium group*5 as the strong bases anion exchange group. H^+ exists as the counter ions of the sulfonic acid group, and OH^- or HCO_3^- exist as the counter ions of the quaternary ammonium group. Both are electrically neutralized. Each ion exchange reaction is as follows:

Cation filter:

$R\text{-}SO_3H + NH_4OH \rightarrow R\text{-}SO_3NH_4 + H_2O$

Anion filter:

$2R\text{-}NOH + H_2SO_4 \rightarrow (R\text{-}N)_2SO_4 + 2H_2O$

SOx, NOx, etc. are listed as the main target gases of the filter for acids removal (strong bases anion type). As an example, the initial removal rate of SOx is shown in Table 5. The filter for bases removal (strong acidic cation type) is used for removal of NH_3 which represents most of the bases. The initial removal rate is approximately 100% as shown in Table 5.

The lifetime of the filter varies largely according to the concentration and velocity of the target gas, thickness of the filter media, etc. Additionally in many cases, the filter is installed in the circulation system and the lifetime of the filter is influenced by the intake quantity of the outer air and quantity of the gas generated internally.

*5: R_4N^+ (R: Alkyl, Aryl, etc.).

Table 5 Initial Removal Performance of the CS Type Chemical Air Filter

	CS type cation filter	CS type anion filter	CS type activated carbon filter
Target gas	NH_3	SO_2	n-decane
Initial removal rate	99% or greater	99% or greater	99% or greater
Inlet concentration	10 μg/m^3	20 μg/m^3	500 μg/m^3 *
Thickness of filter media	60 mm	60 mm	60 mm
Air velocity	0.35 m/s	0.35 m/s	0.35 m/s
Contact time	0.17 s	0.17 s	0.17 s

* n-decane is used as a test gas. The actual target comprises high boiling point organic compounds (DOP, DBP, Siloxane, etc).

Activated Carbon Filter

The CS type activated carbon filter is developed for the removal of condensable organic compounds and has the same features as the previously mentioned ion exchange resin filter. The filter uses a high performance granular activated carbon with a specific surface area of 1500 m^2/g or more. The initial removal rate of n-decane is shown in Table 5.

DOP (Di-octyl Phthalate), DBP (Di-butyl Phthalate), BHT (Butylated Hydroxy-Toluene), etc. are listed as the condensable organic compounds that are apt to adhere to wafers. The molecular weight of DBP is 278, and the boiling point is 341 ℃ (763 mmHg). This compounds is mainly used as a plasticizer.

Other Filters

The PURATEX activated carbon filter is classified into three types: the fiber activated carbon, molding activated carbon, and activated granular carbon, depending on how it is used. The filters all utilize the fine-pore structure and have excellent physical absorption function. Recently the HS (Honeycomb Structure) type activated carbon filter has been developed as the chemical filter for handling hydrogen sulfide following the increase in copper wiring usages.

Measurement of AMC in a Clean Room

The measurement of AMC in a clean room is performed by the combination of the capture method and analysis method as shown in Table 6. Using these measurements, the chemical contamination condition of a clean room cannot be seen in real time except in the case of hydrocarbons. In the table, direct sample introduction is mentioned only for HCA (hydrocarbon automatic measurement method), however, usage of this method is restricted to the locations with a high density of contaminants.

The DT Analyzer for continuous monitoring and measuring of AMC inside a clean room[*6] was developed, applying HORIBA Air Pollution Monitor, AP Series. This device centrically monitors the state of AMC inside a clean room in real time, and additionally it is expected to be used as a monitoring device to determine the lifetime of filters. The main specifications are shown in Table 7.

*6: Refer to "Measurement Technique and its Application to Trace Components of Atmospheric Gas" by Junji Kato, described in this journal.

Table 6 Combination of AMC Capture and Analysis Methods[1]

Capture / Analysis	Impinger [IMP]	Column [SOR]	Filter [FIL]	Syringe [SYR]	Substrate [PSUB] [ASUB]	Canister [CAN]	Direct introduction
Ion chromatography [IC]	A, B, D	—	—	—	—	—	—
Gas chromatography [GC, GC/MS]	—	B (Amin) CD (Organic phosphorus)	—	V	C	C, V	—
High performance liquid chromatography [HPLC]	B	V (HCHO)	B	—	—	—	—
Inductively-coupled-plasma mass spectrometry [ICP-MS]	D, M	—	—	—	—	—	—
Inductively-coupled-plasma atomic emission spectrometry [ICP-AES]	M	—	—	—	—	—	—
Flameless atomic absorption spectrometry [FLAA]	M	—	—	—	—	—	—
Hydrocarbon automatic measuring method [HCA]	—	—	—	—	—	—	V

* [ ] Indicates an abbreviation for the measuring method (a combination of the capture and analysis method).
M: Metals, V: VVOCs

Table 7 Main Specifications of the DT Analyzer

Measurement item	NH_3	NO_X	H_2S	SO_2	O_3
Analysis method	Catalyst oxidization-Chemiluminescence method	Chemiluminescence method	Catalyst oxidization-Ultraviolet fluorescence method	Ultraviolet fluorescence method	Ultraviolet absorption method
Range	0-0.1/0.2/0.5/1.0ppm	0-10/20/50/100ppb	0-10/20/50/100ppb	0-10/20/50/100ppb	0-0.1/0.2/0.5/1.0ppm
Lower limit of detection*	1ppb	0.1ppb	0.1ppb	0.1ppb	0.2ppb
Response time (90%)	5 minutes or less	5 minutes or less	3 minutes or less	3 minutes or less	2 minutes or less
Sample flow rate	Approx. 2.0 L/min	Approx. 1.6 L/min	Approx. 0.8 L/min	Approx. 0.8 L/min	Approx. 0.7 L/min
Peripheral temperature and humidity	0 to 40 ℃, 85% or less	5 to 35 ℃, 85% or less			0 to 40 ℃, 85% or less
Mass	Approx. 46 kg	Approx. 26 kg	Approx. 30 kg	Approx. 20 kg	Approx. 20 kg

* Representative value.

Conclusion

We have outlined airborne molecular contamination control technology as it relates to the semiconductor industry. Of note is that many analyses of chemical contaminants require complicated operations, and therefore there is a need for devices that can carry out measurements simply, accurately, and in a short period of time.
We believe that the DT Analyzer is positioned to satisfy these requirements. However, the possibility of developments such as an automatic trace analyzer for organic substances still remains to be explored. In the future we believe that the development of new technology in cooperation with client companies is indispensable in meeting the needs of the semiconductor industry.

Reference

[1] Japan Air Cleaning Association, Guideline for the notation and analysis of the air cleanliness related to molecular contaminants in a clean room and relevant control environment, JACA No. 35A-2003.

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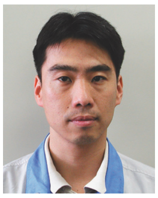

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