

SEMI F5-1101

GUIDE FOR GASEOUS EFFLUENT HANDLING

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NOTICE: This Document, as balloted, is intended to replace SEMI F5-90 in its entirety.

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1 Purpose

- 1.1 The purpose of this Guide is to provide the semiconductor industry with the general knowledge and background information for understanding the principles of exhaust systems.
- 1.2 It includes suggestions for layout and selection as well as application of appropriate methods and equipment for abating emissions.
- 1.3 This Guide is intended for use in abatement selection for both gaseous and particulate contaminant materials potentially emitted from semiconductor manufacturing facilities.

2 Scope

2.1 *Applicability* — This Guide presents a review and evaluation of available information including:

- Chemical and physical properties of chemical compounds and elements, that are, or may be, released from semiconductor manufacturing operations,
- Some current industry practices for separating exhaust systems for different groups of materials,
- Potential methods for abating emissions of gaseous and particulate contaminants exhausted from semiconductor manufacturing operations at 'End-of-Pipe',
- Potential methods for abating emissions of gaseous and particulate contaminants exhausted from semiconductor manufacturing processes at 'Point-of-Use' and reasons why they should be used for some processes,
- Standard industry methods of recovery, replacement, and 'usage reduction' for minimizing release of materials.

2.2 *Contents* — This Document contains the following sections:

1. Purpose
2. Scope
3. Limitations
4. Referenced Standards
5. Terminology
6. Philosophy
7. Classification of Emissions
8. End-of-Pipe Abatement Technologies
9. Point-of-Use (POU) Abatement Technologies
10. Provisions for Emergency Release
11. Summary Table

12. Alternative Approaches

13. Related Documents

Appendix 1 — End-of-Pipe Abatement Design

Appendix 2 — POU Abatement Technology Types

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 This Guide makes only a few recommendations regarding the fire protection aspects of exhaust systems. Additional recommendations on the risk assessment of systems, compatibility of materials, and the potential need for use of non-combustible materials or the fitting of fire detectors, sprinklers etc., are within the scope of other documents.

3.2 Methods for treating solid or liquid waste (created by emission abatement processes) and methods for recovery of gases are not discussed in this document.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI S2 — Environmental, Health, and Safety Guideline for Semiconductor Manufacturing Equipment

SEMI S5 — Safety Guideline for Flow Limiting Devices

SEMI S8 — Safety Guidelines for Ergonomics Engineering of Semiconductor Manufacturing Equipment

4.2 Code of Federal Regulations — United States Environmental Protection Agency¹

40 CFR Part 63 (Clean Air Act 112 (b)(1))

4.3 Uniform Codes²

Uniform Fire Code — Article 80 – Hazardous Material

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 CVD — chemical vapor deposition

5.1.2 EPI — epitaxial deposition

5.1.3 HAP — hazardous air pollutants [as defined by 40 CFR Part 63 (Clean Air Act 112 (b)(1))]

5.1.4 PFC — perfluorocompounds

5.1.5 POU — point of use

5.1.6 VOC — volatile organic compounds

5.2 Definitions

5.2.1 *classification of emissions* — understanding the composition of process exhausts.

5.2.2 *efficiency* — the ratio (or fraction or proportion) of removed chemical species to its input amount.

5.2.3 *end-of-pipe abatement* — abatement technologies that can be fitted at the discharge point of the exhaust system.

5.2.4 *flow capacity* — the maximum flow any specific equipment can handle.

¹ United States Government Code of Federal Regulations, free from the Web site at <http://www.epa.gov>

² International Conference of Building Officials (ICBO), 5360 Workman Mill Road, Whittier, CA 90601-2298, USA

5.2.5 *occupational exposure limits (OELs)* — for the purpose of this document, OELs are generally established on the basis of an eight-hour workday. Various terms are used to refer to OELs, such as permissible exposure levels, Threshold Limit Values®, maximum acceptable concentrations, maximum exposure limits, and occupational exposure standards. However, the criteria used in determining OELs can differ among the various countries that have established values. Refer to the national bodies responsible for the establishment of OELs. (Threshold Limit Value is a registered trademark of the American Conference of Governmental Industrial Hygienists.)

5.2.6 *point-of-use abatement* — abatement technologies that can be fitted at the point of discharge of the gaseous emission from semiconductor process equipment. These devices are also called exhaust conditioners.

5.2.7 *removal capacity* — amount of a species which can be removed.

5.2.8 *usage reduction* — reducing the total volume of process chemicals requiring abatement.

6 Philosophy

6.1 Gaseous mixtures potentially emitted from numerous processes could also produce hazards within exhaust ducts.

6.2 With increasing legal requirements worldwide on both worker safety and general environmental protection, more effective exhaust management is required.

6.3 This demands a detailed understanding of the chemical and physical properties of the chemical compounds being emitted from processes, and of the conditions under which they are released.

6.4 Careful design of the abatement systems is required to attain both high efficiency and maximum economy.

7 Classification of Emissions

7.1 The following fundamental points regarding exhaust emissions should be considered:

- Exhaust contaminants might be solely the material used in the process (e.g., isopropyl alcohol [IPA] from a rinse chamber).
- In plasma and thermal chambers many reactions occur, both those desired and others; therefore, by-products are also key components of exhaust emissions.
- In theory, most possible combinations of the elements in the input gases may be found as compounds in the exhaust. In practice, the main components will be the unused process gas (the percentage consumed in the process varies, and may be as low as 10%). Additional by-products will have different and sometimes more hazardous properties.

7.2 Considerable research has been conducted into various hazardous by-products of processes, from explosive solids to organochlorine compounds with mutagenic properties (see §§ 13.1 through 13.3).

7.3 In considering selection of exhaust systems and abatement technology, it is essential to review all the materials likely to be present in the exhaust.

7.4 Contributions from the materials on the wafer must also be considered, as they often cause blocked exhausts (e.g., aluminum etches produce aluminum chloride [a by-product of removal of aluminum from the wafer with chlorinated gases]).

7.5 Processes that produce specific hazardous by-products should be evaluated for appropriate point-of-use abatement technology before discharge to an exhaust system.

7.6 Gaseous and particulate contaminants emitted from semiconductor manufacturing can be divided conveniently into nine major groups, each of which *might* justify its own exhaust system.

7.6.1 *Group-1 Acid* — Easily hydrolyzable acids, (e.g., hydrogen chloride hydrolyzes into hydrochloric acid.)

7.6.2 *Group-2 Acid aerosols ('difficult-to-scrub')* — This group includes acids that generate aerosols and that are not easily removed by simple water scrubbers (e.g., aqua regia, sulfuric and nitric).

NOTE 1: High concentrations of easily soluble acids will also fall into the 'difficult-to-scrub' category.

7.6.3 *Group-3 Ammonia* — Exhaust streams containing ammonia.

7.6.4 *Group-4 Volatile Organic Compounds (VOCs)* — Exhausts containing volatile organic compound vapors or flammable gas discharge requiring destruction.

7.6.5 *Group-5 Pyrophoric* — Exhausts containing pyrophoric gases.

7.6.6 *Group-6 Emergency Release Discharges* — Enclosures are provided with additional exhausts to contain sudden unanticipated releases of gas from cylinders, etc.

7.6.7 *Group-7 Special/Direct* — Additional exhausts used to keep specific gases separate for recovery purposes (e.g., hydrogen [H₂] reclamation from EPI or PFC reclamation from CVD tools, Oxides of Nitrogen [NO_x]).

7.6.8 *Group-8 General Exhaust Systems Without End-of-Pipe Treatment* — Exhaust of heat or post-treatment exhaust from POU abatement systems.

7.6.9 *Group-9 Highly Toxic Gas Exhaust* — Highly toxic gases especially those with poor warning properties (e.g., arsine, phosphine, diborane, germane). The end user has a primary responsibility to prevent discharge of these gases above a regulated level (e.g., usually one-half [1/2] of Immediately Dangerous to Life and Health [IDLH] levels).

NOTE 2: Facility exhaust systems may be called by a number of different names such as: Acid, Corrosive, Ammonia, Scrubbed, VOC, Solvent, Incinerated, Highly Toxic, Toxic, Dedicated, Special, PFC, General, Heat, Treated, or others. The actual facility exhaust system name, and what groups are routed to each system, will vary by factory and by country.

7.7 The groups listed in § 7.6 are not a definitive division, but represent a summation of common industry practice for separation. The division is based on three basic principles:

- avoiding mixing of incompatible gases in the exhaust,
- potential need for different end-of-pipe abatement technologies, and,
- keeping materials separate for recovery.

7.8 The number of separate exhaust systems used is entirely a decision for each facility, based on the following:

- processes and chemicals used,
- the number of each type of process,
- whether recovery of gases is required,
- whether point-of-use (POU) abatement is installed, and
- compatibility of emissions with each other or the effluent handling system.

7.9 In theory, if POU abatement systems are fitted to all sources of gaseous effluent all exhaust could then be combined into a single exhaust system.

7.9.1 In practice most facilities operate a compromise between the two extremes with two to four separate exhaust systems and point-of-use abatement systems fitted only to certain sources. The decision (as to which combination to use) will often be based on economic and space constraints.

7.9.2 Safety and environmental factors listed below, should always be considered first when determining specific gaseous sources that require POU abatement systems.

7.10 Many types of process equipment use and exhaust incompatible gases sequentially (e.g., silane and then nitrogen trifluoride [NF₃] as elements of a deposition and cleaning cycle).

7.10.1 With more than one of these processes being discharged asynchronously into a common exhaust duct, undesired reactions may occur.

7.10.2 It is possible to avoid this problem by fitting the equipment outlet with three-way valves to divert the discharge to the correct exhaust system, depending on equipment process step. Three-way valves may not be necessary if pump ballast-gas flow is increased to dilute gases.

7.10.2.1 Switching must accurately account for the gas transmission times from process chamber inlet to the exhaust valve.

7.10.2.2 Introduction of additional mechanical devices could create major hazards, reliability, and service or maintenance issues.

7.10.2.3 Valves must incorporate failsafe designs to ensure pump outlet is not shut off.

7.10.3 An alternative solution is to fit a local POU abatement system that treats at least one component and is not adversely affected by the other components.

7.11 POU Abatement Devices

7.11.1 POU abatement devices are designed to operate at the process tool or pump outlet, and to remove hazardous gases BEFORE they enter the exhaust ductwork.

7.11.2 An end-of-pipe scrubber does not protect the facility from reactions in the ductwork. Reactions between process gases, as discussed above, or reactions with other process by-products within the ductwork itself are not prevented by end-of-pipe systems either.

7.11.3 POU abatement devices may be appropriate wherever the exhaust gases can react in the ductwork.

7.11.4 If process systems are not treated with POU abatement devices, the higher concentrations of hazardous gases will present a higher risk during a leak into the facility space.

7.11.5 Improperly functioning POU abatement devices can create backpressure that can increase the risk of a leak.

7.12 Four significant consequences can be foreseen from effluent gas reactions in the ductwork:

7.12.1 *Blocked Ducts* — Reactions between gases, or condensation of vapors, can produce solids and semi-solids (such as crystals, slurries or gels) that will block the ductwork.

7.12.1.1 Collection of solids can create dead leg sections that may contain reactive byproducts or unused raw materials. Catastrophic release of these trapped materials could generate a significant hazard.

7.12.1.2 Extensive downtime (for clean out, or ducts collapsing under the weight of accumulated solids) is a possible undesirable outcome of this condition.

7.12.1.3 Solids deposited (such as from metal etching) can, themselves, be both corrosive and hazardous, leading to health risks for people performing cleaning in ductwork (see Related Documents, §§ 13.1 through 13.3).

7.12.1.4 Blocked ducts may result in toxic process gases or by products escaping into the work area.

7.12.2 *Duct Corrosion* — Etching and some chamber cleaning process emissions are corrosive. Both metallic (including stainless steel) and plastic ducting can be attacked, resulting in the release of hazardous gas or condensed liquids into the workplace.

7.12.3 *Duct Fires or Explosions* — Flammable and pyrophoric gases can ignite in the ductwork. If the ductwork is combustible or has flammable or combustible deposits in it (e.g., hydrocarbon pump oil), facility fires can result.

7.12.4 Additional information on protection of Industrial Exhaust systems from fires may be found in FM Global Loss Prevention Data Sheet 7-78, "Industrial Exhaust Systems".

NOTE 3: Destruction of whole production lines with multi-million dollar cost impact has resulted from such incidents.

7.12.5 *Formation of Ammonium Compounds* — If ammonia is discharged into a duct with acid compounds, a sub-micron ammonium compound fume can be generated, that is not easily removed by end-of-pipe systems.

7.12.5.1 The result is visible discharges.

7.12.5.2 Ammonium compounds produce solids in the duct.

7.13 If any of the above reactions can occur in the process exhaust, POU abatement should be considered.

7.14 Exhausts of oil-lubricated vacuum pumps should be fitted with well-maintained oil mist separators/filters.

7.15 POU abatement devices may also be needed upstream of the recovery device for the recovery of some gaseous compounds (e.g., hydrogen [H₂], PFC gases).

8 End-of-Pipe Abatement Technologies

8.1 Group 1 — Acid Abatement

8.1.1 The appropriate abatement technology for this category is commonly called ‘wet scrubbing’.

8.1.2 Many, if not all, of the semiconductor processes have traditionally been exhausted through centralized wet scrubbers.

8.1.2.1 This procedure has limited technical acceptability and may not meet the requirements of all regulatory agencies.

8.1.2.2 This technology should be targeted at abatement of acid gases, vapors, mists, and fumes emitted from CVD, dry etching, and wet chemical operations.

8.1.2.3 Most wet chemical processes are typically carried out under local exhaust ventilation devices, such as fume hoods, or in specially designed rooms that are totally exhausted. These types of operations include:

- Processes used to clean wafers or clean wafer handling equipment (such as quartz components, tubing),
- Processes used in wafer fabrication for surface treatment such as oxide, silicon nitride and other surface treatments, (e.g., metal etching), and
- Processes used for development of positive photoresist.

8.1.2.4 The chemical species emitted depends on both the chemicals used in the processes and the conditions of use.

8.1.2.5 Volatile acids (e.g., hydrochloric [HCl], hydrofluoric, nitric, and acetic) yield corresponding gases and vapors, especially when heated.

8.1.2.5.1 The reaction of hydrochloric and nitric acids in aqua regia yields nitrosyl chloride (NOCl) vapor and elemental chlorine (Cl₂) gas.

8.1.2.5.2 When sulfuric acid is heated, it yields both sulfuric acid vapor (H₂SO₄) and sulfur trioxide (SO₃).

8.1.2.5.3 Phosphoric acid (H₃PO₄) is not significantly volatile, but spray may be carried over into the exhaust system by mechanical entrainment.

8.1.2.5.4 Under appropriate conditions, spray droplets of any of the chemicals used may be mechanically entrained into the ventilation air exhausted from the various processes.

8.1.3 Design and selection of scrubbing equipment for the acid exhaust systems must take into account both the chemical and physical properties of the materials being emitted.

8.1.4 The principles involved in collection of particulate matter (including liquid aerosols) are entirely different from those determining absorption of gases.

8.1.5 Current Practice

8.1.5.1 Exhausts carrying acid compounds comprise the largest volume of air discharged from a typical semiconductor manufacturing plant.

8.1.5.2 The current practice is to connect most or all of the corrosive sources to a central building exhaust system and to discharge the combined gas streams to one or more large wet scrubbers.

8.1.5.2.1 A variety of scrubber types might be used, but the two main types are cross-flow and counter-current scrubbers equipped with packing material of some type.

8.1.5.3 The scrubbers usually are fed with a stream of water (potable, recycled, etc.).

8.1.5.4 A side stream of water is bled from the scrubber to a wastewater line.

8.1.5.5 It is futile to discharge organic solvents to water scrubbers even if the organic solvents are, to some degree, soluble in water.

8.1.5.5.1 Any dissolved organic solvent will eventually be desorbed from the water and will escape to the atmosphere, or be discharged as wastewater. Additionally, these organics could serve to propagate biological growth in the scrubber.

8.1.5.6 Exhausts from process tools are frequently discharged to the appropriate building exhaust systems, either with or without POU abatement.

8.1.5.7 Arsine and phosphine, which have only slight solubility in water, pass through the water scrubbers so that the effect of discharging these gases into the building scrubber system is limited to dilution. Fluorine and chlorine also have limited solubility in water and may pass through water scrubbers without sufficient abatement. POU abatement devices should be considered for these types of gases.

8.1.5.8 Preliminary oxidation of these and numerous other process gases results in formation of fine fumes and other aerosols that will be collected with only low efficiencies by the typical large, low-energy wet scrubbers.

8.1.5.9 If ammonia is discharged into a system that also carries hydrogen chloride, hydrogen fluoride, nitric acid, or sulfuric acid; it will react, in the vapor phase, to form submicron solid aerosols of ammonium chloride, ammonium fluoride, ammonium nitrate, or ammonium sulfate, respectively.

8.1.5.10 Any exhausts carrying ammonia should be discharged to a separate scrubber or a POU ammonia abatement used at the process discharge.

8.1.6 *Chemistry of Pollutants*

8.1.6.1 Effective abatement of any compound requires careful consideration of the chemistries and physical states of the specific compounds being abated.

8.1.6.2 The packed-bed scrubbers commonly employed should generally be adequate for absorption of readily soluble gases, if appropriate operating conditions are also maintained.

8.1.6.3 Misuse can negate the potential performance of the scrubbers.

8.1.6.4 As scrubbers are low-energy devices (pressure drops on the order of 2.5 to 10 cm (1 to 4 in.) of water, they are incapable of effectively collecting fine aerosols such as the ammonium salts mentioned above.

8.1.6.5 The most economic design approach, therefore, is to arrange the exhaust system and use POU abatement devices to avoid formation of such aerosols, where possible.

8.1.6.6 The practice of using only recirculated water in the scrubber, to absorb acid vapors and to neutralize the water bleed stream should be reviewed to ensure that scrubber efficiency is not affected.

8.1.6.7 Acid gases, such as hydrogen chloride and hydrogen fluoride, are readily soluble in water. The partial pressure of acid gases in equilibrium with the solution, which increases with increasing solute concentration, reduces the absorption of additional gas. Reduction in absorption can be minimized by increasing the rate of water blow-down (i.e., using more fresh water make-up).

8.1.6.8 However, increasing the rate proportionately increases the consumption of water and the volume of water that must be treated before discharge as wastewater.

8.1.6.9 The introduction of an alkaline solution (e.g., sodium hydroxide) in the scrubber can assist in removing compounds from the gas stream if the use of water alone does not provide adequate removal efficiencies. The use of additives in the scrubber can, in itself, create safety and environmental concerns.

8.1.6.10 Some of the neutralized absorbent must be bled off from the recirculated stream to prevent the brine concentration from reaching an excessively high level, but water consumption and the volume of waste can still be reduced by alkaline solution.

8.1.6.11 Aqua regia is a reactive mixture of nitric and hydrochloric acids. The reaction produces nitrosyl chloride and elemental chlorine:



8.1.6.12 The nitrosyl chloride vapor is readily decomposed by absorption in an alkaline solution:



8.1.6.13 Elemental chlorine has only a limited solubility in water, and an alkaline solution (pH > 10) must be used to attain adequate absorption efficiencies:

