

SEMI F5-90

GUIDE FOR GASEOUS EFFLUENT HANDLING

1 Introduction

The manufacturer of semiconductors is responsible for the emission or potential emission of a wide variety of gaseous and particulate contaminants to plant atmospheres and to the general atmosphere. As the resulting hazards become more widely known and understood, such emissions are increasingly coming under legal regulations designed to ensure worker safety and general environmental protection. Effective control of these emissions requires consideration of the chemical and physical properties of the chemical compounds being emitted and of the conditions under which they are released. Careful design of the control systems is required to attain both high efficiency and maximum economy.

2 Purpose

The purpose of this guide is to provide the semiconductor industry with the general knowledge and background information which will assist the industry in selecting and applying appropriate treatment methods and equipment for controlling emission of gaseous and particulate contaminant materials that may present hazards to manufacturing facilities, plant personnel, air quality, or the population at large.

3 Scope

This guide presents a review and evaluation of available information relative to:

3.1 Chemical and physical properties of chemical compounds and elements that are or may be released from semiconductor manufacturing operations.

3.2 Treatment methods for controlling emission of gaseous and particulate contaminants exhausted from semiconductor manufacturing operations.

3.3 Specific control processes that are based on the general treatment methods of (3.2) and the data on contaminant properties from (3.1).

3.4 Types of codes of practice and legal regulations, in force or in preparation, that govern the release of contaminants from semiconductor manufacturing operations.

NOTE: Methods for treating solid or liquid waste created by emission control processes are not discussed in this document.

4 Classification of Emissions and Emission Sources

4.1 The many gaseous and particulate contaminants emitted from semiconductor manufacture can be

grouped conveniently into four major categories (see Table 1). These categories are established basically according to the methods required to control the emissions. The control methods are in turn determined by (1) the chemical and physical properties of the contaminants, and (2) the characteristics of the effluent gas streams carrying the contaminants. In most cases, alternative control processes exist, and the selection of the process to be used is a matter of individual preference. However, not all of the possible alternatives are necessarily of equal merit.

4.2 The acid and caustic gases and mists of Category 1 are generally carried in the exhaust air streams drawn from the fume hoods covering wet sinks and related equipment. Because large volumes of ventilation air have to be exhausted to insure capture of vapors and particles generated in the fume hoods, the aggregate volumes of air drawn from these sources are commonly the largest waste gas streams discharged from semiconductor manufacturing operations. The organic vapors of Category 2 are also commonly contained in air streams drawn from exhaust hoods. The organic vapor-bearing air streams are also relatively large and must be directed to appropriate equipment if effective emission control is to be attained.

4.3 The process exhausts of Category 3 are those discharged from various process tools. They are characteristically very small in gas volume by comparison with the exhaust streams of Categories 1 and 2, but are usually composed almost entirely of gases that are toxic, explosive, or otherwise hazardous. Control methods must be highly specific for the contaminants being discharged.

4.4 The pollutants of Category 4 generally include the same chemical substances that comprise Category 3. However, the circumstances of their release are completely different. Hence, control calls for radically different systems even though the basic processes used may be the same or similar for the two categories.

4.4.1 Category 4 emissions include a variety of releases that may result from accidents, equipment failures, or emergency venting. They may be entirely involuntary or partially controlled. Some may be discharged into exhausted enclosures required by new or existing codes. Others (fugitive emissions) may escape into the general uncontrolled atmosphere either inside or outside the manufacturing plant.

Table 1 Pollutant Emissions from Semiconductor Manufacture

	A	B	C	D	E	F
	<i>Pollutants Emitted</i>	<i>Process Sources</i>	<i>Representative Compounds Emitted</i>	<i>Emission Effects</i>	<i>Applicable Emission Regulations</i>	<i>Applicable Emission Control Processes</i>
1	Acid and Caustic Gases, Vapors, and Mists from Wet Chemical Operations	Cleaning, Etching, Photoresist Stripping	Sulfuric Acid, Hydrochloric Acid, Phosphoric Acid, Nitric Acid, Chlorine, Ammonia, Acetic Acid	Corrosion of Materials and Property, Visible Emissions, Hazard to Personnel	Local Pollution, Control Agency Regulations on Visible Emissions, and General Nuisance	Scrubbing with Alkaline or Acidic Solutions
2	Organic Vapors (Solvents)	Solvent Cleaning and Photoresist Stripping	Isopropanol, Acetone, N-Butyl Acetate, Trichloroethylene, Xylene, Petroleum Distillates, Halocarbons	Hazard to Personnel, Formation of Photochemical Smog and Ozone	Federal, State, and Local Emission Regulations, Uniform Fire Code (UFC)	Adsorption, Catalytic Incineration, Thermal Incineration
3	Toxic, Reactive, and Other Hazardous Gases, Vapors, and Particles from Process Exhaust. Gases Vented During Cylinder Change	Epitaxy, Chemical Vapor Deposition, Diffusion, Ion Implantation, Oxidation, Plasma Etching	Hydrogen, Silane, Arsine, Phosphine, Diborane, Hydrogen Chloride, Phosphorus Tribromide, Dichloro-silane, Phosphorus Oxychloride, Boron Tribromide	Hazard to Personnel, Facilities and Equipment	Federal and State Standards for Industrial Hygiene, Uniform Fire Code (UFC), Uniform Mechanical Code (UMC)	Incineration. Incineration plus filtration. Incineration plus scrubbing. Scrubbing with Alkaline or Oxidizing Solution.
4	Accident or Emergency Releases of Hazardous Gases or Vapors	Equipment Failures, Leaking Gas Cylinders, Pipes, or Valves.	Silane, Phosphine, Diborane, Chlorine, Organometallic Materials, Arsine	Hazard to Personnel, Facilities, and Equipment. Hazard to General Population in Adjacent Areas.	Uniform Fire Codes on Semiconductor Fabrication Facilities and on use and Handling of Hazardous Production Materials	Scrubbing with Alkaline or Oxidizing Solution Plus Filtration

5 Category 1

5.1 Abstract

5.1.1 Category 1 pollutant streams represent the largest proportion of exhausted air within typical semiconductor operations. These pollutants are typically produced from processes such as cleaning, etching, stripping, and/or developing. These processes typically contribute corrosive gases, vapors, or mists to the exhausted air stream.

5.1.2 The appropriate control technology for this category is one that has existed for many years. This method is commonly called "wet scrubbing." Many, if not all, of the semiconductor processes are exhausted through centralized wet scrubbers. However, this

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

5.2 Emission Sources and Chemicals Emitted

5.2.1 The Category 1 pollutants include acid and caustic gases, vapors, mists, and fumes that are emitted from wet chemical operations. Most wet chemical processes are 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:

5.2.1.1 Processes used to clean wafers, wafer handling equipment such as quartz components, tubing, etc.

5.2.1.2 Processes used in wafer fabrication for surface treatment such as oxide, silicon nitride and other surface treatments, metal etching, etc.

5.2.1.3 Processes used for development of positive photoresist.

5.2.2 From the standpoint of the hazards they present, the Category 1 pollutants, which are either acids or bases, are classified as corrosives. The chemicals used in the processes include:

Sulfuric Acid	H ₂ SO ₄
Hydrochloric Acid	HCl
Hydrofluoric Acid	HF
Nitric Acid	HNO ₃
Phosphoric Acid	H ₃ PO ₄
Acetic Acid	CH ₃ CO ₂ H
Aqua Regia	HCl + HNO ₃
Ammonium Hydroxide	NH ₄ OH
Potassium Hydroxide	KOH

5.2.3 The chemical species emitted depend on both the chemicals used in the processes and the conditions of use. The volatile acids (hydrochloric, hydrofluoric, nitric, and acetic) yield corresponding gases and vapors when heated. The reaction of hydrochloric and nitric acids in aqua regia yields nitrosyl chloride (NOCl) vapor and elemental chlorine (Cl₂) gas. When sulfuric acid is heated, it yields both sulfuric acid vapor (H₂SO₄) and sulfur trioxide (SO₃); but when the vapors are cooled by mixture with cool air, they form sulfuric acid mist. Phosphoric acid is not volatile, but some spray may be carried over into the exhaust system by mechanical entrainment. Ammonia gas (NH₃) is evolved from the ammonium hydroxide. However, the potassium hydroxide is not volatile at normal process temperatures, although some spray of the solution may be mechanically entrained.

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

5.2.5 Design and selection of scrubbing equipment for the Category 1 pollutants must take into account both the chemical and physical properties of the materials being emitted. The principles involved in collection of particulate matter are entirely different from those determining absorption of gases.

5.3 Past and Current Practice

5.3.1 The exhausts carrying Category 1 pollutants comprise the largest volume of waste gas discharged from a typical semiconductor manufacturing plant. It

has been conventional practice to connect most or all of the Category 1 sources to a central building exhaust system and to discharge the combined gas streams to one or more large wet scrubbers. The scrubbers usually are fed with a stream of recirculated water. A side stream of water is bled from the recirculated stream to be neutralized with an alkali and then discharged to waste. A variety of scrubber types might be used, but the device most commonly used is a simple countercurrent tower equipped with packings of some type.

5.3.2 Until very recently, it was a common practice to vent all exhausts to the same building exhaust and scrubber system so that pollutants of Categories 1, 2, and 3 were mixed and discharged to the water scrubbers. In varying degrees, this practice is still followed in many existing installations. It is futile to discharge solvent and other organic vapors to the water scrubbers even if the solvents are to some degree soluble in water, as no provision is made for recovering any organic material from the water. Any dissolved solvent will eventually be desorbed from the water and will escape to the atmosphere.

5.3.3 Exhausts from process tools are also frequently discharged to the building exhaust systems, either with or without pretreatment by combustion. Arsine and phosphine, which have only slight solubility in water, will pass through the water scrubbers so that the effect of discharging these gases into the building scrubber system is limited to dilution. Preliminary combustion 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.

5.3.4 If ammonia is discharged into the building exhaust that also carries hydrogen chloride and hydrogen fluoride, it will react in the vapor phase to form submicrometer fumes of ammonium chloride and ammonium fluoride. Again, the typical large wet scrubbers in service will be ineffective on such fumes. Ammonia will also react with nitric acid vapor and sulfuric acid mist to form solid aerosols. Any exhausts carrying ammonia should be discharged to a separate scrubber for collection.

5.4 Chemistry of Pollutants

5.4.1 Effective control of the Category 1 pollutants, like that of the other categories, requires careful consideration of the chemistries and physical states of the specific compounds being controlled. Provided that the correct control chemistry is used, the countercurrent packed tower scrubbers commonly employed should generally be adequate for absorption of readily soluble gases, if appropriate operating conditions are also used.

However, misuse can negate the potential performance of the tower scrubbers. Because they are low-energy devices (pressure drops of the order of 6 inches of water), they are incapable of effectively collecting fine aerosols such as the ammonium chloride mentioned above. The most economic design approach is, therefore, to arrange the control system to avoid formation of such aerosols, where possible.

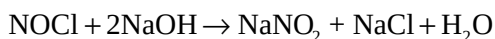
5.4.2 The common practice of using only recirculated water in the scrubber to absorb acid vapors and to neutralize only the water bleed stream is detrimental to the scrubber efficiency. Although such acid gases as hydrogen chloride and hydrogen fluoride are readily soluble in water, the partial pressure of the acid gas in equilibrium with the solution, which increases with increasing solute concentration, reduces the absorption of additional gas. The recirculation also counteracts the benefits of countercurrent flow in the scrubber. These effects can, of course, be reduced by increasing the rate of water bleed-off and using more fresh water makeup. However, this procedure proportionately increases the consumption of water and the volume of acid water that must be treated before discharge to waste. The appropriate procedure is to use not water but a solution of an alkali (sodium hydroxide or sodium carbonate) in the scrubber, adding additional alkali to the spent absorbent stream leaving the bottom of the scrubber before it is recycled to the top of the scrubber. 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 the water consumption and the volume of waste can be limited.

5.4.3 If the effluent gas is ammonia, the same procedure can be employed except that a solution of sulfuric acid should be used as the absorbent.

5.4.4 The preparation and use of aqua regia liberates chlorine gas, which is not readily absorbed in water. Aqua regia is formed by the mixture and reaction of concentrated nitric and hydrochloric acids. The reaction produces nitrosyl chloride and elemental chlorine:



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



Elemental chlorine has only a limited solubility in water, and an alkaline solution must be used to attain adequate absorption efficiencies:



Particularly during the initial reaction of the nitric and hydrochloric acids, hydrogen chloride gas and nitric acid vapor may be volatilized along with the nitrosyl chloride and chlorine. Nitrogen dioxide may also be produced by decomposition of nitric acid. All these compounds can be absorbed in alkaline solution.

5.4.5 If a pollutant is in a particulate form (solid or liquid), its collection is only slightly affected by its chemical nature or solubility. The dominant factor determining its collectability is its particle size.

5.5 Scrubber Design and Selection

5.5.1 Available Scrubber Types

5.5.1.1 A variety of commercially available types of scrubbers are applicable to absorption of the readily soluble gases among the Category 1 pollutants. These include packed tower scrubbers operated in either countercurrent or cocurrent mode, horizontal cross-flow packed scrubbers, horizontal spray chambers, vertical spray towers, and gas-atomizing scrubbers such as the venturi scrubber.

5.5.1.2 To some extent, the choice of scrubber type is a matter of preference, as it is usually possible to obtain equivalent performance on the soluble gases with different types of devices. However, the choice is likely to be limited by a consideration of practical or economic factors such as cost, available space, and weight. For example, it should usually be possible to reduce the size of the scrubber, but at the cost of increased energy consumption.

5.5.2 Gas Absorber Design

5.5.2.1 The principles of gas absorption and methods of design of gas absorption equipment are treated extensively in the chemical engineering literature (Perry and Green, 1984; Treybal, 1980; Sherwood and Pigford, 1952; Sherwood et al, 1975; Norman, 1961; Danckwerts, 1970). The sources cited present rigorous methods for design. However, the practical design of scrubbers is at least semiempirical; and in the case of air pollution control systems, design is often directly based on experimental data. In particular, the prediction of mass-transfer coefficients from theoretical considerations is unsatisfactory despite many years of research by numerous investigators. Consequently, designs should be based on mass-transfer coefficients that have been determined experimentally under, as nearly as possible, the conditions of expected scrubber operation.

5.5.2.2 Rigorous custom design of a scrubber for a particular service requires full knowledge of the conditions that are to be encountered as well as of the performance that is to be attained. By contrast, in the

case of controlling the Category 1 emissions from semiconductor plants, the operating conditions to be encountered are usually poorly defined. The gas flow rate should normally be known fairly accurately — at least when the plant is originally designed. However, the concentrations of the acid and caustic gases are probably seldom estimated accurately, if known at all. Furthermore, the conditions to be met may be changed several times over the probable life of the scrubbing equipment as changes are made in the semiconductor fabrication processes and the exhaust system. The exhaust flow may also be increased, raising the possibility that the scrubber may become overloaded.

5.5.2.3 There is evidently no pool of information on the concentrations of contaminants that may be encountered in typical exhaust gas streams. Furthermore, there appear to be no data generally available on the performance of scrubbers now in service in semiconductor plants. It is questionable how many measurements of performance have ever actually been made. Scrubbers applied to centralized exhaust systems must, of course, receive a variety of contaminants, depending on the kinds of sources being ventilated.

5.5.2.4 The scrubbers being applied to Category 1 pollutants are usually standardized units built by a number of vendor companies. These units are designed to handle specified ranges of gas flow, but in other respects are not designed but simply built. If they are packed scrubbers, they are usually fitted with standard depths of packing. The liquid flow rates can be varied within limits; but otherwise, the performance potentials are fixed unless there are provisions for changing the depth of packing and perhaps the kind of packing. Once the system is installed, such changes to increase the efficiency will probably increase the pressure drop of the scrubber, which will require adding to the fan capacity.

5.5.2.5 To insure in advance that the scrubber will have adequate efficiency, performance tests can be run. Measurements should be made of the contaminant concentrations in typical plant exhaust gas streams, and the resulting data should be used to set conservative performance requirements for the scrubber. Performance tests on the scrubber can be made under laboratory conditions, using a small demonstration unit. The operating variables to be studied in the demonstration unit will, of course, depend upon the type of scrubber being investigated. Solutions of sodium hydroxide should be used as absorbent in all tests for removal of acid gases. Solutions of sulfuric acid should be used as absorbents for ammonia.

5.5.3 Mist Collection

5.5.3.1 Part of the acid emissions may be in the form of mists (fine droplets) rather than gases. These may be composed of the relatively nonvolatile acids such as sulfuric and phosphoric. The mechanisms of removal of particulate matter from gas streams are entirely different from those involved in the absorption of gases (Perry and Green, 1984). The critical factor in the collection process is the particle size of the mist. If the mist is relatively coarse, as apparently is the case in most instances, the same types of scrubbers that are used for gas absorption should collect the mists with adequate efficiency. But if a mist having a particle size in the micrometer or submicrometer range is encountered, it will be necessary to use a high-energy scrubber to obtain adequate collection efficiency. Whenever such a fine mist or other aerosol is encountered, the gas stream from the source should be treated separately from the other exhaust gas streams in the plant so as to minimize energy costs.

5.5.3.2 It has been determined experimentally that the collection efficiency of a scrubber on a given mist or dust is a function of the energy consumed in the gas-liquid contacting process and that the relationship between the energy consumption and the efficiency is little affected by the geometry or size of the scrubber or by the method by which the energy is applied to the contacting process (Perry and Green, 1984). The energy consumption required to attain a given efficiency increases with decrease in the particle size of the mist or dust. In most of the scrubbers used in the semiconductor industry to collect Category 1 pollutants, the energy consumed is drawn from the gas stream in the form of pressure drop.

5.5.3.3 The energy/efficiency relationship provides a convenient and practical method for particle scrubber design. It is essentially independent of the size of the scrubber, at least down to a very small size (perhaps 150 to 300 L/min (5–10 ft³/min) capacity and possibly even smaller). Hence, a small pilot unit can be used to determine performance on an actual plant exhaust stream. Tests can also be made under laboratory conditions, using synthetic aerosols generated for the purpose. The major problem in using synthetic aerosols is in replicating the aerosols actually encountered in practice. The pilot plant scrubber should be tested over a range of pressure drops to give a well-defined pressure drop/efficiency correlation.

5.5.4 Scrubber Selection

5.5.4.1 The design and construction of scrubbers for Category 1 pollutants are simplified by two factors: the exhaust gas streams are at essentially ambient temperature, and they carry few insoluble solids. The