VOLUME II: CHAPTER 6

PREFERRED AND ALTERNATIVE METHODS FOR ESTIMATING AIR EMISSIONS FROM SEMICONDUCTOR MANUFACTURING

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Prepared by:
Eastern Research Group, Inc.

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Denise Alston-Guiden, Galson Consulting
Dennis Beauregard, Co-Chair, Emission Factor and Inventory Group, U.S. Environmental Protection Agency
Bob Betterton, Co-Chair, South Carolina Department of Health and Environmental Control
Paul Brochi, Texas Natural Resource Conservation Commission
Alice Fredlund, Louisiana Department of Environmental Quality
Gary Helm, Air Quality Management, Inc.
Toch Mangat, Bay Area Air Quality Management District
Ralph Patterson, Wisconsin Department of Natural Resources
Jim Southerland, North Carolina Department of Environment and Natural Resources
Eitan Tsabari, Omaha Air Quality Control Division
Bob Wooten, North Carolina Department of Environment and Natural Resources

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INTRODUCTION

The purposes of the preferred methods guidelines are to describe emissions estimation techniques for stationary point sources in a clear and unambiguous manner and to provide concise example calculations to aid in the preparation of emission inventories. This chapter describes the procedures and recommended approaches for estimating air emissions from semiconductor manufacturing operations.

Section 2 of this chapter contains a general description of the semiconductor manufacturing source category, a listing of common emission sources associated with semiconductor manufacturing, and an overview of the available air pollution control technologies for semiconductor manufacturing. Section 3 of this chapter provides an overview of available emission estimation methods. It should be noted that the use of site-specific emissions data is always preferred over the use of industry-averaged data such as default data. However, depending upon available resources, obtaining site-specific data may not be cost effective. Section 4 presents the preferred emission estimation methods for semiconductor manufacturing, and Section 5 presents alternative emission estimation techniques. Quality assurance and quality control procedures are described in Section 6; Section 7 contains data coding procedures. Section 8 identifies the references used to develop this chapter. Appendix A contains an example data collection form for semiconductor manufacturing sources and may be revised to fit individual user's needs.

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SOURCE CATEGORY DESCRIPTION

2.1 PROCESS DESCRIPTION

A semiconductor is a material that has an electrical conductivity between that of a conductor and an insulator; its electrical characteristics can be manipulated to behave like either depending on how it is processed. Silicon has traditionally been the substrate used to manufacture semiconductors. However, the focus in recent years has been on developing valence III-V compounds, such as gallium arsenide (GaAs), as a substrate material. GaAs has several advantages over silicon, such as increased electron mobility and semi-insulating properties (Noyes, 1993).

The semiconductor manufacturing process involves a wide variety of distinct processing steps and is continually evolving. As a result, a range of processes may occur at a single plant and non-uniformity exists for a process design from plant to plant. An average semiconductor manufacturing process consists of hundreds of process steps, a significant percentage of which may be potential air emission sources. Furthermore, many of the manufacturing steps are repeated several times during the production process. This section will discuss general manufacturing steps and does not attempt to describe a specific type of plant.

A clean environment is essential to the manufacture of semiconductors; thus cleaning operations precede and follow many of the manufacturing process steps. Wet processing, during which semiconductor devices are repeatedly immersed in, or sprayed with, solutions, is commonly used to minimize the risk of contamination (EPA, 1995a). These processes also give rise to emissions of a variety of pollutants.

The primary component of a semiconductor is the wafer. The general steps in the semiconductor manufacturing process include wafer preparation, wafer fabrication, and die assembly.

2.1.1 WAFER PREPARATION

Wafers are the starting point for semiconductor production. The wafer is typically made from a single crystal silicon with one of two crystallographic orientations. The substrate is silicon grown from a seed crystal into an “ingot” that is sliced, lapped, etched, and polished to form silicon wafers. Substrate preparation can be accomplished on-site, but is usually completed at other facilities.

In the first step of wafer preparation, ingots are shaped into wafer form through a series of cutting and grinding steps, usually performed using diamond-tipped tools. The ends of the silicon ingots are removed and individual wafers are cut. The wafers may then be polished using an aluminum oxide/glycerin solution to provide uniform flatness in a process called lapping.

This initial shaping of the wafers leaves imperfections in the surface and edge of the wafers that are removed in an etching step. Chemical etching involves the use of hydrofluoric, nitric, or acetic acids as well as alkaline solutions of potassium or sodium hydroxide.

A final polishing step is performed to provide a smooth surface for subsequent processing. In this step, wafers are mounted on a fixture, pressed against a polishing pad under high pressure, and rotated relative to the pad. A polishing slurry, typically containing silicon dioxide particles in sodium hydroxide, is used. This step is both a chemical and mechanical process; the slurry reacts chemically with the wafer surface to form silicon dioxide, and the silica particles in the slurry abrade the oxidized silicon.

In some cases, bare silicon wafers are cleaned using ultrasound techniques, which involve the use of potassium chromate or other mild alkaline solutions (EPA, 1995a).

In the final wafer preparation step, the wafers are usually rinsed in deionized water and dried with compressed air or nitrogen (EPA, 1995a).

2.1.2 WAFER FABRICATION

The basic processes that are utilized in wafer fabrication include photolithography, doping, thin film deposition, etching, metallization, cleaning, and in some cases chemical mechanical planarization. Through the use of physical and chemical processes, hundreds of thousands of miniature transistors are created on the substrate. The result is the formation of integrated circuits on silicon wafers that, when cut into the single “chips,” can be packaged and marketed as separate electronic components to be used in various applications.

The process sequence, equipment, and specific chemicals used in any particular process vary widely. Therefore, the descriptions that follow are for generic types of wafer fabrication processes. The steps outlined below are not meant to represent the order of processing in any wafer fabrication facility. Each of these steps may be used many times in processing a wafer; the number of times each step is repeated is highly dependent on the type of device and its final functional requirements.

Photolithography

Photolithography is used in semiconductor manufacturing to form surface patterns on the wafer through the use of a photoresist. The photoresist is typically a viscous, organic solvent-based material which reacts to the presence of light. This process allows various materials to be deposited at or removed from selected, precise locations. In this process, an adhesion promotor is first applied to the wafer surface to help the photoresist stick to the silicon wafer. A fixed amount of photoresist is then applied to the wafer using a high speed rotating element to uniformly coat the wafer surface. In most cases an edge bead removal (EBR) step is performed to remove any beads of photoresist on the edge of the wafer.

After a “soft bake” to remove most of the carrier solvent, a pattern is introduced into the photoresist by exposing predefined areas of the wafer with specific wavelengths of light, lasers, electron beams, or other means. This may be accomplished through the use of a template mask, which is a glass plate containing an image of the desired circuit.

Finally, a photoresist developer is applied to remove unwanted portions of the photoresist, thereby yielding a stencil for further processing. Depending on the photoresist system, the exposed areas become more or less soluble in the developer solution. If a negative photoresist is used, the exposed areas polymerize (harden), while the photoresist unpolymerizes when positive resists are used.

The “patterned” wafer allows for further processing (etching, ion implant, etc.) to ultimately give a printed circuit. After the subsequent processing steps, residual photoresist is removed by wet stripping (solvent or acid) or plasma gas stripping. The number of photolithography steps performed on an individual wafer varies, depending on the type and complexity of the integrated circuit device being produced.

One of the most common adhesion promotors is hexamethyldisilizane. Typical examples of chemicals used in photoresist coating and EBR processes include propylene glycol monomethyl ether acetate (PGMEA), ethyl lactate, n-butyl acetate, methyl isobutyl ketone, n-hexane, toluene, and xylene(s). Photoresist developers for negative resists are typically solvents such as xylenes or mineral spirits; developers for positive photoresists are typically very dilute solutions of tetramethyl ammonium hydroxide in water. Typical solvent based strippers contain amines Such as N-methyl 2 pyrollidone, typical acid based strippers contain sulfuric acid, and plasma stripping usually employs oxygen and simple perfluorocarbons (PFCs).

Doping

Doping is a process whereby atoms of specific impurities are introduced into the silicon substrate to alter the electrical properties of the substrate by acting as charge carriers. The concentration and type of the dopant atoms dictate the electrical characteristics that define the functionality of the transistor, and ultimately, the device. Doping is typically accomplished through ion implantation or diffusion processes.

Ion implantation is the most common method used to introduce impurity atoms into the substrate and provides a more controlled doping mechanism than diffusion. The dopant atoms are first ionized with a medium- to high-current filament, then accelerated toward the wafer surface with large magnetic and electrical fields. Precise control of the dopant ion momentum in this process allows for precise control of the penetration into the silicon substrate. Because of the high kinetic energy of the ions during bombardment, damage to the crystalline structure of the substrate occurs. To restore the structure of the substrate to a satisfactory level, slow heating or "annealing" of the amorphous material in various gaseous atmospheres is subsequently performed.

Diffusion is a high-temperature process also used to introduce a controlled amount of a dopant gas into the silicon substrate. The process occurs in a specially designed tube furnace where dopants may be introduced in one of two primary ways:

- Gaseous diffusion - dopant gases may be introduced into the furnace that will diffuse into the exposed areas of the substrate; or

- Non-gaseous diffusion - or dopant atoms may diffuse into the substrate from a previously deposited dopant oxide layer in the areas where the two are in contact.

By knowing the amount of dopant atoms and using a carefully controlled constant temperature, a predictable solid-state diffusion may be achieved.

Typical examples of chemicals used in doping processes include compounds of antimony, cobalt, indium or other group IIIa or Va elements, as well as gases such as arsine, phosphine, boron trifluoride and diborane.

Thin Film Deposition

In thin film deposition, layers of single crystal silicon, polysilicon, silicon nitride, silicon dioxide, or other materials are deposited on the wafer to provide desirable properties on portions of the device or to serve as masks. Each of these films serves a specific purpose in device operation:

- Single crystal silicon films (also called epitaxial silicon) serve as the substrate in which the heart of transistors are constructed;

- Amorphous silicon films (also called polysilicon) serve as gate electrodes in most modern devices; these films are typically heavily doped to make them very conductive;

- Silicon nitride films serve as passivation layers that are used primarily as protective layers after most device processing has occurred, but may also be used as an etch stop; and

- Silicon dioxide films are deposited by oxidation processes and are by far the most frequently deposited films. Silicon dioxide films act primarily as dielectric layers, but may also act as masks for subsequent processing.

Oxidation processes may be dry or wet, and occur in high-temperature furnaces (>600°C). In the furnace, the silicon wafer surface oxidizes with steam (i.e., wet oxidation) or a gas such as oxygen (i.e, dry oxidation) to form a silicon dioxide layer. Generally, wet oxidation does not involve the use of regulated pollutants. In the dry oxidation process, however, a chlorine source (chlorine gas, anhydrous hydrochloric acid, or trichloroethylene) may be used to alter oxide characteristics.

Deposition of thin films is also frequently performed in chemical vapor deposition (CVD) reactor chambers or high-temperature tube furnaces. CVD processes use silicon-containing gases as reactants and sometimes employ selected impurity compounds (dopants) to alter the electrical characteristics of the deposited film or layer. Diffusion furnaces are, by design, very high throughput tools, are typically run at very high temperatures (1,000°C), and can be run at atmospheric or low pressure. Because of the high temperatures, diffusion processes are normally used most frequently before any metals are deposited on the wafer. Reactor chambers can be batch or single wafer tools, and typically have lower throughput than diffusion furnaces. They are typically run at lower temperatures (500°C), and low pressure. Deposition in reactor chambers may be enhanced by striking a plasma in the chamber to overcome kinetic barriers. This allows for rapid deposition without the use of elevated temperatures, which is important for processing steps after metals are deposited on the wafer.

Inorganic acids and organic solvents may be used to clean furnaces between batches or to clean reactor chambers after a prescribed number of wafers are processed. Halogenated gases may be used to clean reactor chambers or furnaces between wafers or between batches.

Silicon-bearing reactants (such as silane, tetraethylorthosilicate [TEOS], dichlorosilane, trichlorosilane, silicon tetrachloride and others) may be used with or without nitrogen-and oxygen-containing gases (such as ammonia or nitrous oxide) in deposition of various film types. Where they are used, the dopant gases are similar to those used in doping processes. For deposition of metal films, the silicon-containing reactant gases are replaced with metal-containing reactant gases such as tungsten hexafluoride. Gases used to clean reactor chambers between runs include hexafluoroethane and nitrogen trifluoride.

Examples of chemicals used in these deposition processes include ammonia, 1,2-dichloroethylene, cobalt, copper, and hydrochloric acid.

Etching

Etching of the silicon substrate or deposited film is used to chemically remove specific areas of the substrate or film so that an underlying material is exposed or another material may be deposited in place of the etched material. Etch processes usually occur after a photoresist pattern has been applied, so that the etching is accomplished in specific areas.

Etching may be performed by the following processes:

- Wet etch - using solutions of acids, bases, or oxidizers; or
- Dry etch - uses various gases (usually halogenated) excited by striking a plasma .

Dry etching provides a higher resolution than wet etching, generally produces less undercutting of the wafer substrate, and is more likely to be used as circuit elements become smaller. In either case, the fluoride ion or radical is almost always introduced if the substrate or film to be etched contains silicon.

Examples of chemicals used in wet etch processes are hydrofluoric acid (sometimes buffered with ammonium fluoride), phosphoric acid, nitric acid and acetic acid. Plasma etch gases used for silicon films include PFCs such as hexafluoroethane, tetrafluoromethane, trifluoromethane, nitrogen trifluoride and sulfur hexafluoride. Gases used for plasma etch of metal films include chlorine and boron trichloride.

Metallization

To interconnect electrical devices on an integrated circuit and to provide for external connections, metallic layers (usually aluminum) are deposited onto the wafer by evaporation, sputtering (also called physical vapor deposition or PVD), or chemical vapor deposition. Evaporation consists of vaporizing a metal under a vacuum at a very high temperature. Sputtering processes involve bombarding metallic targets with a plasma gas, which displaces ions from the target and deposits them on the wafer. Chemical vapor deposition of metal is similar to the other deposition processes described in the Thin Films section, except that the reactive gas is a metal-containing vapor. Devices may have a single layer or multiple layers of metal.

The use of copper as a replacement for aluminum is under investigation by many companies. Copper metallization may be accomplished by CVD or PVD methods as described above, or by electrolytic or electroless plating.

Examples of chemicals used in PVD metallization processes include argon as the plasma gas, and aluminum as the deposited metal. CVD metallization processes typically use gases such as tungsten hexafluoride.

Cleaning

Cleaning of the wafers is required to prepare them for each chemical and physical process to ensure that contaminants on the wafer surfaces do not affect the electrical performance of the final integrated circuit. Wafers may be cleaned before, and sometimes after, they are subjected to any specialized manufacturing processes, they are typically immersed in or sprayed with various aqueous and/or organic solutions, and in some cases mechanically scrubbed in some manner to remove films, residues, bacteria, or other particles. Two basic types of tools are widely used in various cleaning applications: wet hoods and spray tools. Fog chambers may be used for wafer cleaning in some cases.

Examples of chemicals used in cleaning processes include a wide variety of inorganic acids, ammonium hydroxide, various alcohols, and various amines.

Chemical Mechanical Planarization

Chemical mechanical planarization (CMP) is used in semiconductor manufacturing to remove the top layer of material from the wafer in a controlled manner, leaving a smooth, flat surface for further processing. There are two major applications of this technology. The first is to selectively remove the top part of a layer or film to reduce the topography on the wafer (also called planarization). This is normally performed on the nonconducting layers. The end result is an increase in the process margin for both deposition and photolithography. The second use is removal of excess material from the surface. This is normally performed on conducting layers (metals). After a blanket pattern, conducting material is deposited on the underlayer, and the wafer is polished down to the patterned underlayer. The result is a smooth, flat surface that has conducting material left in the patterned crevices.

As the name implies, CMP slurries are composed of two components; a chemical component to react with the film on the wafer surface, and a mechanical component to abrade the reacted surface layer and remove it. Typical chemical components include bases such as potassium hydroxide and oxidizers such as ferric nitrate or hydrogen peroxide. Typical mechanical components are very fine (submicron) silica and alumina particles.

2.1.3 SEMICONDUCTOR ASSEMBLY

The final steps in the assembly of semiconductors involves:

- Testing each chip (i.e., die);
- Mounting the functional chips onto a protective enclosure (i.e., package);
- Electrically connecting the chips to packages; and
- Enclosing the chips within the packages to protect them.

Protective enclosures may be made from plastic, ceramic, or other materials; however, plastic is most commonly used (EPA, 1995a). Marking, and in some cases metal finishing, processes may follow the encapsulation steps to make the packaged chip easy to install in the final consumer product.

The packaging process typically employs solvents such as isopropyl alcohol, acetone, and terpenes to clean chips and packages prior to connection. Depending on the packaging technology, aqueous metal plating solutions may be used to prepare the chip for connection to the package, or to prepare the packaged chip for installation in the consumer product.

2.2 EMISSION SOURCES

The physical and chemical processing steps discussed in Section 2.1 occur at three general types of process areas:

- Wet chemical stations such as those used for wafer cleaning and wet etch;
- Coating application stations such as those used in photolithography; and
- Gaseous operation stations such as those used in etching, thin film deposition, and doping.

A variety of pollutants may be emitted at these stations. These include acid fumes and organic solvent vapors from cleaning, rinsing, resist drying, developing, and resist stripping; hydrogen chloride, hydrogen fluoride, and vapors from etching; and other various vapors from spent etching solutions, spent acid baths, and spent solvents (EPA, 1995a).

In addition to process-related emissions, air emissions may also result from on-site treatment of industrial wastewater. Potential liquid wastes include rinse water containing acids and organic solvents from cleaning, developing, etching, and resist stripping processes; rinse water from aqueous developing systems; spent etching solutions; spent solvents; and spent acid baths. For a discussion of air emissions from industrial wastewater collection and treatment, refer to Chapter 5 of this volume.

If fossil fuel fired boilers and generators are used, criteria pollutant emissions will be generated. Criteria pollutants may also be emitted from the combustion of organic pollutants in control devices. Refer to Chapter 2 of this volume for estimating emissions from boilers and other combustion sources.

2.2.1 WET CHEMICAL STATIONS

Wet chemical stations are used to clean wafers, remove resist, and etch patterns into silicon or metal. Materials used during the wet process may include acids (sulfuric, phosphoric, nitric, hydrofluoric, and hydrochloric), solvents (various alcohols, glycol ethers, amines), oxidizers (hydrogen peroxide), bases (ammonium hydroxide), and other solutions.

There are generally two types of tools used for wet chemical processes: wet hoods and spray tools. Wet hoods have a sequence of open or covered tanks with various chemicals, usually with a dedicated rinse tank for each chemical tank. The wafers travel through each chemical bath and rinse in proper sequence, until the clean, etch or strip process is complete. Spray tools typically have one or two dedicated chambers for the wafers, into which various chemicals (and subsequent rinses) flow or are sprayed in sequence until the clean, etch or strip process is complete. Wet hoods use time- or throughput-based chemical dumps. Spray tools may use time- or throughput-based dumps, or may use chemicals only once then dump to drain. The two tools may have very different emissions characteristics for identical chemical use, and the nature of the emissions from each tool type is strongly dependent on the way the tool is operated.

Wet chemical stations of any type generally emit acids, bases or solvents to an exhaust system. Depending on the emission rate and concentration, conventional emissions control technology can be employed to reduce emissions where necessary.

2.2.2 COATING APPLICATIONS

Coating applications include any process where materials are applied to wafers using track equipment or other mechanical means. This would include photoresists, developers, rinse solutions, spin on glass, edge bead removers, adhesives, resins, etc. Emissions occur as these materials are applied, either through evaporation or atomization (aerosols).

For example, once the resist material has been spun onto the wafer, solvents in the resist are evaporated by baking the wafer at low temperatures. During the lithography step, developers are used that may also cause emissions.

Because of the critical nature of lithography steps in wafer processing, all of these chemicals are typically used once then routed to drains. This scenario makes emission rates linearly proportional to chemical use rates.

Coating applications stations typically emit solvents and sometimes bases to an exhaust system. Depending on the emission rate and concentration, conventional emissions control technology can be employed to reduce emissions where necessary.

2.2.3 GASEOUS OPERATIONS

Many of the processes at semiconductor manufacturing facilities occur in gaseous environments, and most are in the cleaning, doping, plasma etching, and thin film deposition areas. Specific processes include atmospheric and low pressure CVD, plasma-enhanced CVD, ion implantation, diffusion, plasma etching, plasma/ion etching, and plasma resist stripping.

Because the process feeds are primarily gaseous, emissions from these processes are normally higher on a percent of inlet feed basis than for wet chemical processes. However, the absolute emissions are normally much lower because of the relatively small amount of chemicals used. Emissions for some very reactive chemicals may be nearly zero as they are consumed in the process or in the exhaust system prior to discharge. Emissions of very stable chemicals may approach the inlet feed rate, as very little chemical utilization is achieved in the process. The emission rates for each chemical, tool and process will depend on many factors (flow, pressure, temperature, coupled RF or microwave power, geometry, etc.), but is typically linear with the process feed rates of the chemicals.

In dry chemical stations, PFC gases such as carbon tetrafluoride and hexafluoroethane are used for etching wafers and cleaning reactors in plasma processes. The PFC gases in the reactor chamber form fluorine species, including hydrogen fluoride (HF). However, the conversion of PFC gases to HF is incomplete, and a complete accounting of each fluorine species is difficult to obtain. The mixture of gaseous products exhausted from the reactor chamber may contribute significantly to the total HF emissions from a semiconductor manufacturing facility.

Gaseous operations stations emit a wide variety of chemicals to an exhaust system. Some of these chemicals may be easy to remove with conventional air pollution control systems, but many pose unique challenges. Compounds such as PFCs are very stable and have very low water solubility, and are not removed to any appreciable extent by conventional treatment. Compounds such as silane and phosphine are very reactive and may start fires in an exhaust system, so must be treated as quickly as possible. The industry's approach to reducing emissions from these processes is widely varied, and continues to evolve in response to improving new control technologies.

2.2.4 MISCELLANEOUS OPERATIONS

In addition to the major chip production and cleaning processes, there are usually other miscellaneous processes occurring at a semiconductor manufacturing facility which may result in emissions. These would include wipe cleaning, equipment maintenance and assembly, and final mark and pack operations associated with packaging the product for distribution. Typically these processes are minor as far as contribution to facility-wide emissions, but should be accounted for in a complete inventory assessment.

2.3 PROCESS DESIGN AND OPERATING FACTORS INFLUENCING EMISSIONS

Emissions from semiconductor manufacturing processes may be affected by many different process, equipment design, and air pollution control equipment parameters. This section describes process equipment design, control devices, and chemical substitution methods. In some cases, adjustment of these parameters can be used to reduce the amount of pollutant-containing material used, as well as to reduce emissions from those pollutant-containing materials that are used.

2.3.1 PROCESS MODIFICATIONS

Process modifications are changes in equipment design or operating practices employed to reduce emissions. For example, open-top vapor cleaners (OTVCs) are often used for cleaning of electronic components (EPA, 1993). Air currents within an OTVC can disturb the vapor zone and cause excessive solvent emissions. Some machines have covers of varying design to limit chemical losses and contamination during downtime or idling. Additional control of the chemical vapor is provided by the freeboard, which is that part of the tank wall extending from the top of the solvent vapor level to the tank lip. The freeboard reduces the effect of room draft (EPA, 1993).

Emissions from these machines are also influenced by the solvent-air interface area, which equals the surface area of the cleaning tanks. Machines that do not expose the cleaning solvent to the ambient air during or between the cleaning of parts, such as vacuum-to-vacuum machines, do not have a solvent-air interface. These systems operate in a closed loop and the solvent is not exposed to the air outside of the machine (EPA, 1995b).

Emissions from batch vapor and in-line machines can be reduced with covers on the machine openings. Covers should be closed whenever possible to minimize vapor loss. For machines without covers, vapor emissions can be decreased by reducing room draft. This can be accomplished by increased freeboard height and slower parts handling (e.g., hoist speed). Primary condensers on vapor cleaning machines consist of liquid- or gas-chilled cooling coils that condense rising solvent vapors. To effectively reduce emissions, primary condensers must be maintained to create a controlled vapor zone. Lip exhausts, used to reduce worker exposure to solvents, dramatically increase overall solvent air emissions if there are no control devices (EPA, 1995b).

Except for inlets and exits for parts, in-line conveyors are almost always enclosed to reduce solvent losses (EPA, 1993).

2.3.2 CONTROL DEVICES

Because of the need for an ultra-clean manufacturing environment and to ensure worker protection, a relatively large amount of air is exhausted from a typical wafer fab. The semiconductor manufacturing industry in general is characterized by very dilute concentrations of pollutants in very high flow exhaust streams. The low concentrations give only low driving forces for separation, and can make high removal efficiency difficult. The exhaust streams are usually segregated to some degree, so that appropriate emissions control can be applied to the corresponding pollutants. Air pollutant emissions may be controlled through the use of add-on control devices or point-of-use control systems.

Add-on Controls

Add-on control devices are used to control emissions once they are generated. They may be designed to destroy pollutants (such as through combustion) or to recover them for reuse or recycling off-site (as with adsorption or absorption). Zeolite rotor concentrators may be used to concentrate dilute streams of organics prior to sending them to a destruction or recovery device.

Scrubbers are typically employed to control acid or base emissions, and thermal oxidizers or adsorbers are used to control organic solvent emissions. Additionally, semiconductor facilities use a “burn box” to safely control emissions of pyrophoric and toxic gases such as silane and phosphine. Such burn boxes may or may not use supplemental fuels.

A prototype system has been recently developed for concentration and recovery of PFC gases (Tom et al., 1994). Using a dual-bed adsorber, activated carbon is used in a PFC concentrate and recovery unit (CRU). In this system, concentrated PFC gases are sent to one bed in adsorption mode while the other bed is regenerated, evacuated by vacuum, and then recompressed. This method can produce recycled gases of 97 percent concentration; however, in an initial test of this system, the percentage of unreacted PFCs (i.e., “leakage” through the bed) gradually increased to 30 percent due to fluctuating bed temperatures. Other technologies for treating PFC emissions are currently under development as well.

Table 6.2-1 lists add-on control technologies commonly found at semiconductor manufacturing plants.

Point-of-Use Control (POU) Systems

Point-of-use (POU) control systems are designed for treating air emissions from the outlet of the semiconductor process to remove the compounds of interest and prevent them from entering the main exhaust ductwork. Only recently has reduction of air emissions been a consideration in the use of POU control systems. Historically, POU control systems have been installed for reducing production downtime and for health and safety reasons. Typically, POU control systems are interlocked with the process equipment (i.e., when a POU control system fails, the process equipment is shut down). The main reasons for the use of POU control systems are as follows:

- Prevent exhaust restrictions (blocked ductwork) - reactions between gases, solids from the process, or condensation of vapors produce solid build-up in ductwork. This build-up can cause production downtime to clean ductwork, repair collapsed ductwork, etc. An additional issue is the handling and disposal of these solids during and after removal.

TABLE 6.2-1

ADD-ON CONTROL TECHNOLOGIES EMPLOYED AT SEMICONDUCTOR FACILITIES

Control Technology	**Pollutant**	**Comments**
Horizontal wet scrubbers (cross flow)	Acids or Bases	Can have bypass problems with poor design. Will not remove mists of particulates smaller than 5μm.
Vertical wet scrubbers (counter flow)	Acids or Bases	Will not remove mists of particulates smaller than 5μm.
Regenerative thermal oxidizers	VOCs	Prone to static pressure instability due to frequent air path switching.
Zeolite rotor concentrators with recuperative thermal oxidizers	VOCs	Zeolite type and capability is variable and should be selected based on inlet stream composition to maximize destruction/removal efficiency.
Fluidized bed polymer adsorption with recuperative thermal oxidizer or hot nitrogen regeneration	VOCs	Increased bed fires can result from poor desorber performance. If regeneration is used, waste is generated that may be burnable for heat recovery off-site.
Fixed bed carbon adsorption with steam stripping	VOCs	Carbon bed fires are a risk due to ketones used. Waste is generated that may be burnable for heat recovery off-site.
Fluidized bed carbon adsorption with hot nitrogen desorption	VOCs	Waste is generated that may be burnable for heat recovery off-site.

- Prevent ductwork fires/explosions - flammable (hydrogen, etc.) and pyrophoric (silane, etc.) gases are used in semiconductor equipment and can cause a fire and/or explosion in the ductwork, possibly resulting in major facility damage and personnel injury.

- Prevent duct corrosion - etching gases (chlorine, etc.) and byproducts (i.e., hydrogen chloride from boron trichloride) can corrode metal ductwork and other materials of construction. This results in production downtime and possible personnel exposure to these gases in the area outside of ductwork.

- Prevent exposure to personnel - toxic gases (hydrides, chlorine, etc.) are controlled near the semiconductor equipment outlet to reduce the likelihood that any toxic gases can migrate into the area outside ductwork where personnel are located.

- Prevent ammonium compounds formation - ammonia will react with acid compounds (hydrogen chloride, nitric acid, etc.) to form ammonium compounds (ammonium chloride, ammonium nitrate, etc.). These ammonium compounds will aggregate in the ductwork and possibly generate a sub-micron particle visible opacity at the stack outlet (generally at 1 ppmv or greater at stack outlet).

- Comply with air regulatory requirements - emissions limits may need to be met in specific regulatory jurisdiction that require POU control systems to be used. Some of this need is due to the lower removal efficiencies for compounds of interest at the centralized ("end-of-pipe") scrubbers (e.g., chlorine).

Table 6.2-2 lists suggested POU technologies for 14 semiconductor applications. These applications were compiled from a survey of nine semiconductor suppliers (Sherer, 1996).

TABLE 6.2-2

POU CONTROL SYSTEM TECHNOLOGIES FOR VARIOUS SEMICONDUCTOR MANUFACTURING APPLICATIONS

Application	POU[a] Control System Technologies
Wet clean hood with NH_4OH/H_2O_2 bath	Wet scrubbing (with chemical addition)
Wet spray etcher with aqua regia	Wet scrubbing (with chemical addition)
Epitaxial silicon with hydrogen vented	Wet scrubbing (without chemical addition)
Epitaxial silicon with hydrogen abated	Oxidation with hydrogen present/wet scrubbing
Ion implant	Cold bed
Poly deposition; non-PFC[b] clean	Oxidation using electric/wet scrubbing; or oxidation using fuel/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing
Doped poly deposition; PFC clean	Oxidation using electric/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing
Metal etch (aluminum)	Cold bed; or hot chemical bed; or wet scrubbing (high pH) control with chemical addition
Nitride deposition with silane; PFC clean	Oxidation using electric/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing
Nitride deposition with dichlorosilane; PFC clean	Hot chemical bed/ammonia control system; or oxidation using electric/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing (with low pH control with chemical addition)
Oxide deposition; PFC clean	Cold bed; or hot chemical bed; or oxidation using electric/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing
Tungsten deposition; PFC clean	Cold bed; or hot chemical bed; or oxidation using electric/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing; or wet scrubbing only (if low silane removal is acceptable)
Poly etch	Cold bed; or hot chemical bed; or wet scrubbing
BPSG[c] oxide deposition; PFC clean	Hot chemical bed; or oxidation using electric/wet scrubbing; or pre-pump reactor and post-pump wet scrubbing

[a] POU = Point of Use
[b] PFC = Perfluorocarbons
[c] BPSG = Boron phosphorous silicon glass
Source: Sherer, 1996

2.3.3 CHEMICAL SUBSTITUTION

Solvent substitution is the replacement of pollutant-containing materials with less volatile, or pollutant-free materials that serve the same function. Process substitution is similar, but instead of an alternative material, a different process is used to obtain the same result. For example, in some cases, dry stripping of resists using only oxygen (in a plasma) can be substituted for wet stripping of resists which use solvents such as N-methyl 2 pyrrolidone.

One manufacturer found that total solvent cleaning usage was decreased significantly by replacing broad spectrum cleaning solvents and mixtures (i.e., one cleaner for all contaminants) with lesser amounts of contaminant-specific cleaning agents (Shire, 1994).

Another manufacturer evaluated several classes of cleaning solvents to replace trichloroethylene usage in the assembly process and found *d*-limonene, a terpene cleaning solvent, was a satisfactory substitute (Meier, 1993). Yet another manufacturer of wafers modified the cleaning, stripping, and photoresist processes to reduce usage of xylenes, and 1,2,4-trichlorobenzene by 33 percent while eliminating usage of chlorofluorocarbons (CFCs) and 1,1,1-trichloroethane (1,1,1-TCA). Xylene usage was decreased by replacing polyisoprene-based negative photoresist with a conventional, propylene glycol monomethyl ether acetate (PGMEA)-based positive resist and, more recently, with negative-tone I-line photoresists (Shire, 1994). Consequently, PGMEA-based photoresists have successfully replaced ethylene glycol ether-based resists at this same facility (Shire, 1994). CFC-113 usage for vapor degreasing was replaced with a high-pressure water jet/detergent-type “dishwasher” that is also used for cleaning wafer trays and cassettes (Shire, 1994).

Criteria considered in selection of an alternate cleaning solvent may include:

- Compatibility with existing solvent cleaning stations (e.g., aqueous cleaning could not be substituted for existing heated bath cleaning);
- Flash point (e.g., high flash points for heated baths);
- Odor;
- Soils loading (e.g., cured photoresist); and
- Cost (i.e., initial and disposal) (Shire, 1994).

Additional quality considerations in solvent substitution include material compatibility, corrosion resistance, cleaning effectiveness, product quality, and manufacturing efficiency (Meier, 1993).

Temperature and agitation are two specific parameters that affect the effectiveness of cleaning solvents at cleaning stations. Substitution of a solvent used for wax removal may also require selection of a replacement wax that is soluble in the solvent and has a similar consistency and melting point as the original wax.

3

OVERVIEW OF AVAILABLE METHODS

3.1 EMISSION ESTIMATION METHODOLOGIES

Several methodologies are available for calculating emissions from semiconductor manufacturing processes. The best method to use depends upon available data, available resources, and the degree of accuracy required in the estimate. In general, site-specific data that are representative of normal operations at a particular site are preferred over data obtained from other similar sites, or industry-averaged data. This section discusses the methods available for calculating emissions from semiconductor manufacturing operations and identifies the preferred method of calculation on a pollutant basis. A comparison of the methods is also presented.

3.1.1 MATERIAL BALANCE

A material balance approach may be used to estimate emissions when the quantities of a material used, recycled, and disposed of are known. For liquid applications, such as wet chemical stations or coating/solvent application stations, usage figures would typically be in gallons. The difference (by mass) of the amount of a liquid used and the amount of the liquid recovered, either through product recovery or disposal, is assumed to equal releases to the air.

Similarly, estimating emissions for gaseous operations would require knowledge of pollutant-containing gas usage. Annual usage may be based on gross purchased amount (in cubic feet.) Normally, only those gases that are considered hazardous or toxic air pollutants (or which can generate them) would need to be considered. However, some states define air hazardous pollutants very broadly, so gaseous compounds such as perfluorocompounds may also need to be tracked even if they do not appear on the Federal HAP list.

When operations have several recipes for different batches, a conservative emissions estimate for each pollutant may be developed based on the recipe with the highest pollutant usage. It should be noted that no waste is typically collected from gaseous operations which may make a complete material balance difficult to determine.

3.1.2 EMISSION FACTORS

Emission factors are used to estimate emissions based on known relationships between process rates and emission rates, or between chemical use and emission rates. The use of emission factors to estimate emissions from semiconductor manufacturing facilities is an appropriate approach. Development of an accurate emission factor would require detailed knowledge of the process conditions and chemical usage rates during the time period for which emissions are known. Emission factors should be applied to similar-type processes utilizing similar or identical chemical recipes.

3.1.3 SOURCE TESTS

While technologies such as gas chromatography (GC), mass spectrometry (MS), and infrared spectroscopy (IS) may be available for use at semiconductor manufacturing facilities (Strang et al., 1989), data are not available to evaluate their actual use in this industry. One study stated that fourier transform infrared (FTIR) monitors may be appropriate for quantitative monitoring of selected compounds at semiconductor facilities (Strang et al., 1989), and work is currently being done to validate this technique.

EPA has published test methods for determining air emissions in Title 40 CFR Part 60, Appendix A. Methods that would be applicable to semiconductor manufacturing would be Method 18 (speciated organics), Method 25 (volatile organic compounds or VOCs), and Method 0030 (speciated organics).

Recently, work has been completed by Sematech, a consortium of U.S. semiconductor manufacturers, to develop a source test and analytical procedure using gas chromatography/mass spectrometry (GC/MS) and FTIR designed specifically to estimate air emissions from semiconductor manufacturing. Several companies have recently used this type of method for quantifying emissions from individual manufacturing tools. The method utilizes a quadrupole mass spectrometer to perform in-line sampling at the exhaust line coming directly out of the process tool or physical processing unit (Higgs, 1996).

3.1.4 ENGINEERING CALCULATIONS

In the absence of other data, engineering calculations may be used to estimate emissions from some processes. For example, for any process that involves transfer of a chemical species from the liquid phase to the vapor phase, the saturation (equilibrium) vapor pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that process. This is a conservative approach because of the assumption that the total airflow is saturated. A typical air dilution to saturation ratio may be assumed to be as high as 800 to 1.

An alternative method, based on mass transfer kinetics, is presented in the EPA document *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Form* (EPA, 1987). This approach does not assume airflow saturation and results in a lower emission rate estimate than would be obtained assuming saturation.

3.2 COMPARISON OF AVAILABLE EMISSION ESTIMATION METHODOLOGIES

Table 6.3-1 identifies the preferred and alternative emission estimation approaches for the primary types of pollutants emitted at semiconductor manufacturing facilities. The preferred method for estimating organic compound (VOC and HAP) emissions is through the use of a material balance. It should be noted that while this method would result in an accurate estimate, each fate of the chemical must be known. It should also be noted that determining individual organic HAPs through mass balance may not be feasible if the HAP in question makes up a very small portion of the total VOC stream. This approach is appropriate for estimating emissions from solvent stations, cleaning stations, and processes where solvents evaporate. The preferred method for estimating emissions of inorganic HAPs (especially acids and other chemical process-related byproducts) is through the use of source testing. In using source testing data, it must be understood that semiconductor fab emissions can be highly variable, so caution must be used in attempting to scale up a short term source test in an annual emissions estimate.

TABLE 6.3-1

SUMMARY OF PREFERRED AND ALTERNATIVE EMISSION ESTIMATION METHODS FOR SEMICONDUCTOR MANUFACTURING OPERATIONS

Pollutant	Preferred Emission Estimation Approach	Alternative Emission Estimation Approaches
VOC (total)	Material Balance	Source Testing Engineering Calculations Emission Factors[a]
Speciated Organics (including HAPs, toluene, xylenes, ethylbenzene, CFCs, PFCs)	Material Balance	Source Testing Engineering Calculations Emission Factors[a]
Inorganic HAPs (acids, bases)	Source Testing	Engineering Calculations Emission Factors[a]

[a] Emission factors obtained using site-specific source testing data are preferred over those obtained from other sources.

Emission factors and engineering calculations may be based on sources other than site-specific data and should only be used if one of the preferred methods is not a viable alternative due to lack of data or resources. It is possible to obtain high-quality emissions estimates using emission factors, but only if they were developed at the facility in question, or a similar facility, using one of the preferred methods mentioned above.

3.2.1 MATERIAL BALANCE

A material balance approach is the preferred method for estimating emissions of VOCs, including specific HAPs (xylene, ethylbenzene, toluene, etc.) from solvent stations and other solvent sources. This approach is suitable for these types of pollutants because they are not involved in chemical reactions. Also, their usage and waste rates may already be tracked for purchasing reasons as well as other non-air-related environmental reporting purposes.

For other pollutants emitted at semiconductor manufacturing facilities, a material balance may not be appropriate due to the uncertainty in the extent of chemical reactions occurring. For example, while hydrofluoric acid is used in baths and spray tools, it is also formed from the use of PFCs (carbon tetrafluoride, hexafluoroethane, sulfur hexafluoride, and nitrogen trifluoride) in dry etching and CVD processes. In addition no waste is collected from many of these processes, so a material balance cannot be performed in the same manner that is done with VOCs.

In addition, many of the processes occurring in the semiconductor manufacturing industry occur in radio frequency plasma environments. This makes it very difficult to determine the origin and fate of all the chemical species involved.

3.2.2 EMISSION FACTORS

Emission factors may be also be used to estimate emissions from semiconductor manufacturing. However, because of the highly variable nature of the semiconductor manufacturing process, whenever possible, emission factors should be determined using site-specific data. There are three principal ways to derive emission factors for semiconductor manufacturing operations:

- Through the use of emissions test data (preferably performed at tool exhausts);
- Use of a material balance approach; or
- Use of engineering calculations.

Once derived, these factors may be applied to estimate emissions based on production ratios or other appropriate parameters (e.g., usage rates of a particular chemical). This approach provides an alternative method of estimating emissions over a longer term or for a different processing scenario based on short-term emission estimates (i.e., during the time of the test) obtained from individual process steps. Emission factors for one process may be appropriate to use for estimating emissions from similar processes occurring within a facility or at other similar facilities.

3.2.3 SOURCE TESTS

Standard EPA test methods may be used to obtain emission estimates from semiconductor manufacturing processes for specific classes of compounds. However, because of the nature of the exhaust streams found in semiconductor manufacturing facilities (high flow and low pollutant concentration), emissions are often below reliable detection limits of standard tests (Higgs, 1996). FTIR methods are able to detect multiple pollutants simultaneously, and FTIR is being used currently in this industry. The EPA Method 301 validation has been performed successfully for this technology.

It should be noted that short-term source testing is often used to develop site-specific emission factors, which are in turn used to develop long-term emission estimates. In most cases this is the preferred method for estimating emissions. For semiconductor facilities, this method should use tool-specific source tests. This is because end of pipe emission rates may be difficult to correlate to tool-specific chemical usage rates due to a large number of tools vented to a single stack. Tool-specific emission factors may then be combined to develop an overall, weighted average emission factor for an entire facility.

3.2.4 ENGINEERING CALCULATIONS

In the absence of sufficient data to apply one of the other methods, engineering calculations may be used to estimate organic compound (VOC and/or HAP) and inorganic HAP emissions. Engineering calculation approaches are based on theoretical equations and not measured values, and are the least preferred of the options discussed within this document. However, for some operations, such as hooded acid baths, an estimate of emissions can be calculated using the evaporation rate equation. Engineering calculation approaches are justified where no other approaches are economically or technically feasible.

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4

PREFERRED METHODS FOR ESTIMATING EMISSIONS

The preferred method for estimating VOC and speciated organic emissions (including HAPs) from semiconductor manufacturing processes is the use of a material balance. This approach can be used to estimate emissions of pollutants not involved in chemical reactions from solvent, coating application, and wet chemical stations. Material balance uses the raw material usage rate and material disposal rate (present in product or waste streams) to estimate emissions.

The preferred methods for estimating inorganic HAP emissions (e.g., acids) are the use of source testing or engineering calculations.

The equations and examples in this section present how material balance and source testing data may be used to estimate VOC, speciated organic, and speciated inorganic emissions. Table 6.4-1 lists the variables and symbols used in the following discussions.

TABLE 6.4-1

LIST OF VARIABLES AND SYMBOLS

Variable	Symbol	Units
Total emissions of pollutant x	E_x	typically lb/hr; also ton/yr
Material entering the process	Q_{in}	gal/hr
Material leaving the process as waste, recovered, or in product	Q_{out}	gal/hr
Concentration of pollutant x	C_x	parts per million by volume dry (ppmvd) or lb/gal
VOC content of material	C_{VOC}	lb/gal
Total VOC emissions	E_{VOC}	lb/hr
Density of material	d	lb/gal or lb/ft^3

TABLE 6.4-1

(CONTINUED)

Variable	Symbol	Units
Percentage by weight of pollutant x in material	$wt\%_x$	%
Molecular weight of pollutant x	MW_x	lb/lb-mole
Stack gas volumetric flow rate	V	dry standard cubic feet per hour (dscf/hr)
Molar volume	M	cubic feet (ft^3)/lb-mole
Annual emissions of pollutant x	E_a	ton/yr
Operating hours	OH	hr/yr

4.1 EMISSIONS CALCULATION USING MATERIAL BALANCE

Material balance is the preferred method for estimating emissions of VOCs and organic HAPs used in semiconductor manufacturing as carrier solvents, cleaners, etc. VOC emissions from semiconductor manufacturing may be estimated using a material balance approach by applying Equation 6.4-1:

$$E_x = (Q_{in} - Q_{out}) * C_x \qquad (6.4\text{-}1)$$

where:

E_x = Total emissions of pollutant x (lb/hr)
Q_{in} = Material entering the process (gal/hr)
Q_{out} = Material leaving the process as waste, recovered, or in product (gal/hr)
C_x = Concentration of pollutant x (lb/gal)

The term Q_{out} may actually involve several different "fates" for an individual pollutant. This could include the amount recovered (or recycled), the amount leaving the process in the product, the amount leaving the process in the wastewater, or the amount of material shipped off-site as hazardous waste. Complete information of the different fates for the pollutant of interest is necessary for an accurate emissions estimate. Example 6.4-1 illustrates the use of Equation 6.4-1.

Example 6.4-1

This example shows how VOC emissions may be calculated using Equation 6.4-1 for a cleaning process given the following data:

Q_{in} = 2 gal/hr
Q_{out} = 1.5 gal/hr
C_{VOC} = 7.5 lb VOC/gal

$$\begin{aligned} E_{VOC} &= (Q_{in} - Q_{out}) * C_{VOC} \\ &= (2 \text{ gal/hr} - 1.5 \text{ gal/hr}) * 7.5 \text{ lb VOC/gal} \\ &= 3.75 \text{ lb VOC/hr} \end{aligned}$$

Speciated VOC emissions may be estimated by a material balance approach using Equation 6.4-2:

$$E_x = (Q_{in} - Q_{out}) * d * (wt\%_x)/100 \qquad (6.4\text{-}2)$$

where:

E_x = Total emissions of pollutant x (lb/hr)
Q_{in} = Material entering the process (gal/hr)
Q_{out} = Material leaving the process as waste, recovered, or in product (gal/hr)
d = Density of material (lb/gal)
$wt\%_x$ = Percentage by weight of pollutant x in material (%)

Example 6.4-2 illustrates the use of Equation 6.4-2.

Example 6.4-2

This example shows how toluene emissions may be estimated for a cleaning process using toluene-containing solvent given the following data:

Q_{in} = 2 gal/hr
Q_{out} = 1.5 gal/hr
d = 7.5 lb/gal
wt%$_x$ = 25% toluene

E_x = $(Q_{in} - Q_{out}) * d * (wt\%_x)/100$
= (2 gal/hr - 1.5 gal/hr) * 7.5 lb/gal * 25/100
= 0.94 lb/hr

4.2 EMISSIONS CALCULATION USING SOURCE TEST DATA

Pollutant-specific test methods can be used to estimate inorganic HAP emission rates from semiconductor manufacturing (e.g., EPA Office of Solid Waste (OSW) Method 9057 for Hydrochloric Acid (HCl)).

Sampling test reports often provide chemical concentration data in parts per million by volume dry (ppmvd).

If the concentration is known, an hourly emission rate can be determined using Equation 6.4-3:

$$E_x = (C_x * MW_x * V)/(M * 10^6) \tag{6.4-3}$$

where:

E_x = Total emissions of pollutant x (lb/hr)
C_x = Concentration of pollutant x (ppmvd)
MW_x = Molecular weight of pollutant x (lb/lb-mole)
V = Stack gas volumetric flow rate (dscf/hr)
M = Molar volume; i.e., volume occupied by 1 mole of ideal gas at standard temperature and pressure (385.5 ft^3/lb-mole at 68°F and 1 atm)

Please note that Equation 6.4-3 calculates emissions per hour. The equation is valid for any time period as long as consistent units are used throughout. This example equation is intended to show how an emission rate may be obtained from volumetric flowrate and pollutant concentration data. Airflow rates can be determined from flow rate meters or from pressure drops across a critical orifice (e.g., EPA Method 2).

Emissions in tons per year can be calculated by multiplying the average hourly emission rate (lb/hr) from Equation 6.4-3 by the number of operating hours (as shown in Equation 6.4-4 below) or by multiplying an average emission factor (lb/gal) by the total annual amount of material used (gal). If emissions in tons per year are calculated from an average hourly rate, it is beneficial to have multiple hourly data points to average. Since emissions from semiconductor manufacturing processes fluctuate, no single hourly measurement can be assumed to be representative of the average hourly emissions over a year.

$$E_a = E_x * OH * 1 \text{ ton}/2{,}000 \text{ lb} \qquad (6.4\text{-}4)$$

where:

E_a = Annual emissions of pollutant x (ton/yr)
E_x = Total hourly emissions of pollutant x (lb/hr)
OH = Operating hours (hr/yr)

Example 6.4-3 illustrates the use of Equations 6.4-3 and 6.4-4.

Concentration data obtained from testing may be presented in a variety of units, including parts per million (ppm) or grams per dry standard cubic feet (g/dscf), and in a variety of conditions, such as wet, dry, or excess O_2. Conversion of concentration data to consistent units may be required for compatibility with the equations given above.

Example 6.4-3

This example shows how annual hydrogen fluoride (HF) emissions can be calculated using the data obtained from an emissions test. The concentration of HF is provided, hourly emissions are calculated using Equation 6.4-3, and annual emissions are calculated using Equation 6.4-4.

Given:

$C_{a,x}$ = 15.4 ppmvd (measured as F^-)
MW_x = 20.0 lb/lb-mole of HF
V = 109,020 dscf/hr
OH = 1,760 hr/yr
M = 385.5 ft^3/lb-mole
2,000 = 2,000 lb/ton

Hourly emissions are calculated using Equation 6.4-3:

$$E_x = (C_x * MW_x * V)/(M * 10^6)$$
$$= 15.4 \text{ ppmvd} * 20.0 \text{ lb/lb-mole} * 109{,}020 \text{ dscf/hr}/(385.5 \text{ ft}^3/\text{lb-mole} * 10^6)$$
$$= 0.09 \text{ lb/hr}$$

Annual emissions are calculated using Equation 6.4-4:

$$E_a = E_x * OH * 1 \text{ ton}/2{,}000 \text{ lb}$$
$$= 10.09 \text{ lb/hr} * 1{,}760 \text{ hr/yr} * 1 \text{ ton}/2{,}000 \text{ lb}$$
$$= 0.08 \text{ ton HF/yr}$$

5

ALTERNATIVE METHODS FOR ESTIMATING EMISSIONS

Source testing, engineering calculations, and emission factors are alternative methods for estimating organic compound emissions (including VOC and HAP). Engineering calculations and emission factors are alternative methods for estimating emissions of inorganic HAPs.

The following equations and examples present how emission factors and engineering calculations may be used to estimate VOC, speciated organic, and speciated inorganic emissions. Table 6.5-1 lists the variables and symbols used in the following discussions.

TABLE 6.5-1

LIST OF VARIABLES AND SYMBOLS

Variable	Symbol	Units
Concentration of pollutant x	C_x	ppmvd or lb/gal
Total emissions of pollutant x	E_x	typically lb/hr
Molecular weight of pollutant x	MW_x	lb/lb-mole
Stack gas volumetric flow rate	V	dscf/hr
Molar volume	M	ft^3/lb-mole
Annual emissions of pollutant x	E_a	ton/yr
Operating hours	OH	hr/yr
Emission factor for pollutant x	EF_x	lb/units
Activity factor	AF	units/hr
Saturation vapor pressure of pollutant x	$P_{sat,x}$	atmosphere (atm)
Total pressure of pollutant x	P_t	atm

TABLE 6.5-1

(CONTINUED)

Variable	Symbol	Units
Density of pollutant x	d_x	lb/gal or lb/ft^3
Evaporation rate of pollutant x	W_x	lb/sec
Gas-phase mass transfer coefficient	K	ft/sec
Surface area	A	ft^2
Vapor pressure of pollutant x	$P_{vap,x}$	pounds per square inch absolute (psia)
Ideal gas constant	R	psia * ft^3/degrees Rankine (°R) * lb-mole
Temperature	T	°R
Wind speed	U	miles/hr

5.1 EMISSIONS CALCULATION USING SOURCE TEST DATA

Various pollutant-specific stack sampling test methods can be used to estimate VOC and speciated organic emission rates from semiconductor manufacturing. Pollutant concentration data can be obtained using grab sample methods (e.g., EPA Method 18) and airflow rates can be determined from flow rate meters or from pressure drops across a critical orifice (e.g., EPA Method 2).

Sampling test reports often provide chemical concentration data in parts per million by volume dry (ppmvd).

If the concentration is known, an hourly emission rate can be determined using Equation 6.5-1:

$$E_x = (C_x * MW_x * V)/(M * 10^6) \qquad (6.5\text{-}1)$$

where:

E_x = Total emissions of pollutant x (lb/hr)

C_x = Concentration of pollutant x (ppmvd)
MW_x = Molecular weight of pollutant x (lb/lb-mole)
V = Stack gas volumetric flow rate (dscf/hr)
M = Molar volume; i.e., volume occupied by 1 mole of ideal gas at standard temperature and pressure (385.5 ft^3/lb-mole at 68°F and 1 atm)

Please note that Equation 6.5-1 calculates emissions per hour. The equation is valid for any time period as long as consistent units are used throughout and is intended to show how an emission rate may be obtained from volumetric flowrate and pollutant concentration data.

Emissions in tons per year can be calculated by multiplying the average hourly emission rate (lb/hr) from Equation 6.5-1 by the number of operating hours (as shown in Equation 6.5-2 below) or by multiplying an average emission factor (lb/gal) by the total annual amount of material used (gal).

$$E_a = E_x * OH * 1 \text{ ton}/2{,}000 \text{ lb} \qquad (6.5\text{-}2)$$

where:

E_a = Annual emissions of pollutant x (ton/yr)
E_x = Total hourly emissions of pollutant x (lb/hr)
OH = Operating hours (hr/yr)

Example 6.5-1 illustrates the use of Equations 6.5-1 and 6.5-2.

Concentration data obtained from testing may be presented in a variety of units, including parts per million (ppm) or grams per dry standard cubic feet (g/dscf), and in a variety of conditions, such as wet, dry, or excess O_2. Conversion of concentration data to consistent units may be required for compatibility with the equations given above.

Example 6.5-1

This example shows how annual toluene emissions can be calculated using the data obtained from a process emissions test. The concentration of toluene is provided, hourly emissions are calculated using Equation 6.5-1, and annual emissions are calculated using Equation 6.5-2.

Given:

C_x = 15.4 ppmvd
MW_x = 92.0 lb/lb-mole of toluene
V = 109,020 dscf/hr
OH = 1,760 hr/yr
M = 385.5 ft^3/lb-mole
2,000 = 2,000 lb/ton

Hourly emissions are calculated using Equation 6.5-1:

$$\begin{aligned} E_x &= (C_x * MW_x * V)/(M * 10^6) \\ &= 15.4 \text{ ppmvd} * 92.0 \text{ lb/lb-mole} * 109{,}020 \text{ dscf/hr}/(385.5 \text{ ft}^3/\text{lb-mole} * 10^6) \\ &= 0.40 \text{ lb/hr} \end{aligned}$$

Annual emissions are calculated using Equation 6.5-2:

$$\begin{aligned} E_a &= E_x * OH * 1 \text{ ton}/2{,}000 \text{ lb} \\ &= 0.40 \text{ lb/hr} * 1{,}760 \text{ hr/yr} * 1 \text{ ton}/2{,}000 \text{ lb} \\ &= 0.35 \text{ ton toluene/yr} \end{aligned}$$

5.2 EMISSIONS CALCULATION USING EMISSION FACTORS

Emission factors may be used to estimate VOC, organic HAP, and inorganic HAP emissions from semiconductor manufacturing operations using Equation 6.5-3:

$$E_x = EF_x * AF \tag{6.5-3}$$

where:

E_x = Emissions of pollutant x (lb/hr)
EF_x = Emission factor for pollutant x (lb/units)

AF = Activity factor (units/hr)

Example 6.5-2 illustrates the use of Equation 6.5-3. It should be noted that *AP-42* does not contain emission factors for semiconductor manufacturing, and emission factors will need to be developed specific to the processes or operations of interest. Emission factors are generally developed from process-specific sampling or engineering calculations and may be expressed as a function of production or a function of total chemical use. The activity factor may be expressed in terms of production units or amount of chemical used per unit time.

Example 6.5-2

The emission factor used in this example was developed with site-specific data from a semiconductor manufacturing facility. This example shows how HF emissions may be calculated using emission factors and Equation 6.5-4 given the following data:

EF_{HF} = $6.0 * 10^{-6}$ lb HF/wafer
AF = 30 wafers/hour

$$
\begin{aligned}
E_{HF} &= EF_{HF} * AF \\
&= 6.0 * 10^{-6} \text{ lb HF/wafer} * 30 \text{ wafers/hr} \\
&= 1.8 * 10^{-4} \text{ lb HF/hr}
\end{aligned}
$$

5.3 EMISSIONS ESTIMATION USING ENGINEERING CALCULATIONS

For any process that involves transfer of a chemical species from the liquid phase to the vapor phase, the saturation (equilibrium) vapor pressure and exhaust flow rate from the process can be used to establish the upper limit of emissions from that process through the use of Equation 6.5-4:

$$E_x = (P_{sat,x}/P_t) * V * d_x \tag{6.5-4}$$

where:

E_x = Emissions of pollutant x (lb/hr)
$P_{sat,x}$ = Saturation vapor pressure of pollutant x (atm)
P_t = Total pressure (atm)
V = Stack gas volumetric flow rate (dscf/hr)
d_x = Density of pollutant x

Example 6.5-3 illustrates the use of Equation 6.5-4.

Example 6.5-3

This example shows how methanol emissions may be estimated from a hooded process using Equation 6.5-5 given the following data:

$P_{sat,x}$ = 0.13 atm
P_t = 1 atm
V = 6,000 dscf/hr
d_x = 0.083 lb/ft^3

$$E_{methanol} = (P_{sat,x}/P_t) * V * P_x$$
$$= (0.13 \text{ atm}/1 \text{ atm}) * 6{,}000 \text{ ft}^3/\text{hr} * 0.083 \text{ lb/ft}^3$$
$$= 64.7 \text{ lb methanol/hr}$$

The approach used in Equation 6.5-4 provides an extremely conservative estimate of emissions due to the assumption of airflow saturation. As mentioned previously, a dilution to saturation ratio (based on testing) may be applied to this equation to provide a more realistic estimate of pollutant concentration.

EPA has published an alternative method in the document *Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release and Inventory Form* (EPA, 1987), which is based on mass transfer kinetics. For this alternative, use Equation 6.5-5:

$$W_x = (MW_x * K * A * P_{vap,x})/(R * T) \qquad (6.5\text{-}5)$$

where:

W_x = Evaporation rate of pollutant x (lb/sec)
MW_x = Molecular weight of pollutant x (lb/lb-mole)
K = Gas-phase mass transfer coefficient (ft/sec)
= $0.00438 * U^{0.78} * (18/MW_x)^{1/3}$
U = Wind speed (miles/hr)
A = Surface area (ft^2)
$P_{vap,x}$ = Vapor pressure of pollutant x (psia)
R = Ideal gas constant (10.73 psia * ft^3/°R * lb-mole)

T = Temperature (°R)

Example 6.5-4 illustrates the use of Equation 6.5-5.

Example 6.5-4

This example shows how methanol emissions from semiconductor manufacturing may be estimated using mass transfer kinetics and Equation 6.5-6 given the following data:

MW_x = 32 lb/lb-mole
U = 1.7 miles/hr
A = 1 ft^2
$P_{vap,x}$ = 1.91 psia
T = 533°R
R = 10.73 psia * ft^3/°R * lb-mole

First, calculate the mass transfer coefficient, K:

$$
\begin{aligned}
K &= 0.00438 * U^{0.78} * (18/MW_x)^{1/3} \\
&= 0.00438 * (1.7 \text{ miles/hr})^{0.78} * (18/32 \text{ lb/lb-mole})^{1/3} \\
&= 0.00547 \text{ ft/sec}
\end{aligned}
$$

Then, calculate W_x:

$$
\begin{aligned}
W_x &= (MW_x * K * A * P_{vap,x})/(R * T) \\
&= (32 \text{ lb/lb-mole} * 0.00547 \text{ ft/sec} *1 \text{ ft}^2 * 1.91 \text{ psia})/(10.73 \text{ psia} \\
&\quad \text{ft}^3/533^\circ\text{R} * \text{lb-mole})(533^\circ\text{R}) \\
&= 5.84 * 10^{-5} \text{ lb/sec}
\end{aligned}
$$

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6

QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance (QA) and quality control (QC) are essential elements in producing high quality emission estimates and should be included in all methods used to estimate emissions. QA/QC of emissions estimates is accomplished through a set of procedures that ensures the quality and reliability of data collection and processing. These procedures include the use of appropriate emission estimation methods, reasonable assumptions, data reliability checks, and accuracy/logic checks of calculations. Volume VI of this series, *Quality Assurance Procedures*, describes methods and tools for performing these procedures.

In addition, Chapter 1 of this volume, *Introduction to Stationary Point Source Emission Inventory Development*, provides QA/QC guidance for preparing point source emission estimates. The following sections discuss QA/QC considerations that are specific to the emission estimation methods presented in this chapter for estimating emissions from semiconductor manufacturing.

6.1 QA/QC FOR USING MATERIAL BALANCE

The material balance method for estimating emissions may use various approaches; the QA/QC considerations will also vary and may be specific to an approach. Generally, the fates of all materials of interest are identified, and then the quantity of material allocated to each fate determined. Identifying these fates, such as material contained in a product or material leaving the process in the wastewater, is usually straightforward. However, estimating the amount of material allocated to each fate may be complicated and is the prime QA/QC consideration in using the material balance approach. Amounts obtained by direct measurement are more accurate and produce emission estimates of higher quality than those obtained by engineering or theoretical calculations. QA/QC of an emissions estimate developed from a material balance approach should include a thorough check of all assumptions and calculations. Also, a reality check of the estimate in the context of the overall process is recommended.

6.2 QA/QC FOR USING EMISSION FACTORS

When using emission factors to estimate emissions from semiconductor manufacturing, the applicability and representativeness of the emission factor are the first criteria to consider. To assess applicability, the reviewer needs to examine how closely the process of interest matches the process for which the emission factor is available. Similarly, the reviewer should look at how well the range of conditions on which the available emission factor is based compares to the conditions of interest. For example, an emission factor that is based on a process rate of 100 wafers per hour may not be the best emission factor to use for a process rate of 10 wafers per hour.

6.3 QA/QC FOR USING SOURCE TEST DATA

In reviewing stack sampling or FTIR data, the first consideration is whether the method measures the pollutant of interest or can only be used as a surrogate. For example, if fluorine concentration in a hood exhaust is measured, HF emissions could be estimated only after assuming all, or a given percentage, of the fluorine is present as HF. Next, the reviewer should determine whether the sampling conditions represent the operating conditions of interest for the emission estimate. For example, if the data are to be used to estimate emissions during typical operations, then sampling should have been done during typical operating conditions.

The accuracy of source testing data depends heavily on maintaining calibration. Thus, the reviewer should evaluate the calibration information. Parameters that should be evaluated in QA/QC of stack sampling data and the acceptance criteria for stack sampling are presented in Chapter 1 of this volume.

6.4 QA/QC FOR USING ENGINEERING CALCULATIONS

In most cases, engineering calculations are less accurate than the other methods for estimating emissions due to the lack of any site-specific measurement data. In the case of the approaches outlined for semiconductor manufacturing, the calculations are based on theoretical equations that were developed independent of the source. In certain cases, engineering calculations may be presented in the form of an emissions model that has been calibrated for an individual source by using emissions estimates from one of the preferred calculation approaches (in Section 4.0). For example, plasma chemistry models could be used to determine the percentage of fluorine present in PFCs converted to HF.

6.5 DATA ATTRIBUTE RATING SYSTEM (DARS) SCORES

One measure of emission inventory data quality is the DARS score. Chapter 4 of Volume VI, *Quality Assurance Procedures*, and the QA/QC section in Chapter 1 of this volume provide a complete discussion of DARS. DARS assumes activity data and factor data are used to generate an inventory and provides criteria that are used to assign a numerical score to each data set. The activity score is multiplied by the factor score to obtain a composite score for the emissions estimate. The highest possible value for an individual or composite score is 1.0. The composite score for the emissions estimate can be used to evaluate the quality and accuracy of the estimate.

DARS was used to evaluate the methods for estimating emissions that are presented in this document to provide an idea of the relative quality of each method. This was accomplished by assuming an inventory was developed using each method and using DARS to score each inventory. Because the inventories are hypothetical, it was necessary to make some assumptions. The first three assumptions were that emissions are for a 1-year period, from one process or from one facility, and for normal operating conditions. Also, all material usage data used were assumed to be reasonably accurate. Some scores are expressed as a range, with the lower value representing an estimate developed from low- to medium-quality data and the upper value representing an estimate based on relatively high-quality data. Tables 6.6-1 through 6.6-4 present the DARS scores for the different emission estimation methods presented in this chapter. It should be noted that the DARS scoring is currently applied manually, but the system will eventually be publicly available as a software tool.

Comparing the scores for the different methods, the preferred methods (material balance and source testing) received the highest scores and the alternative methods (emission factors and engineering calculations) received the lowest. The material balance method for estimating emissions received the highest DARS score (0.98), as shown in Table 6.6-1. Note that the score is based on the assumption that the factor data were measured intermittently during the year (the inventory period). Also, note that if factor data and activity data are measured continuously over the year, a perfect score (1.0) is possible for an emissions estimate when using material balance.

The source testing approach received the next highest overall score (0.78-0.93), as shown in Table 6.6-2. As indicated by the scores, the major parameters affecting the quality of stack sampling data are the number of tests (range of loads; numerous tests performed over the year) and the frequency of measurement of activity data (intermittent or continuous). A high DARS score for an emissions estimate based on stack sampling data is possible if the factor data are the result of numerous tests performed during typical operations and the activity data are the result of continuous measurements over the inventory period.

In using DARS to score the emission factor approach, the example provided shows how the representativeness (or quality) of an emission factor may vary and how emission factor quality affects emission estimates. The example shown in Table 6.6-3 assumes the emission factor was developed from a process that is similar, if not identical, to the process for which the emissions estimate was made. Because the emission factor represents a process similar to the inventory process, a high score is assigned. Assuming the activity data were measured continuously, a composite score of 0.83 to 0.90 results. The lower value reflects the score assigned to an estimate based on a lower-quality emission factor and the upper value reflects an estimate based on a higher-quality emission factor. As shown by the scores in Table 6.6-3, the quality of an emissions estimate developed from emission factors is directly affected by the quality of the emission factors and can vary greatly. The scores also indicate that a source-specific emission factor may produce an emissions estimate of higher quality than an estimate developed from a factor developed for a similar process.

For engineering calculations, the DARS score of 0.68 to 0.86 results, as shown in Table 6.6-4. The main parameter lowering the score is the Source Specificity parameter, which has low scores for both the Factor Score and the Activity Score. This is because the equations were calculated independently of the actual source. Although it is hard to define the Spatial and Temporal Congruity attributes for this method, a score of 0.9 to 1.0 was assigned because the approaches presented would not vary temporally or spatially.

The examples provided in the tables are given as an illustration of the relative quality of each estimation method. If DARS was applied to actual inventories developed using the preferred and alternative methods and data of reasonably good quality were used for each method, the scores could be different; however, the relative ranking of the methods would be expected to remain the same.

TABLE 6.6-1

DARS SCORES: MATERIAL BALANCE DATA[a]

Attribute	Factor Score	Activity Score	Emissions Score	Factor Assumptions	Activity Assumptions
Measurement/Method	0.9	0.9	0.81	Factor is based on accurate data.	Intermittent measurement of activity.
Source Specificity	1.0	1.0	1.0	Factor developed specifically for the intended source.	Activity data represent the emission process exactly.
Spatial Congruity	1.0	1.0	1.0	Factor developed for and specific to the given spatial scale.	Activity data developed for and specific to the inventory area (one process).
Temporal Congruity	1.0	1.0	0.95	Factor developed for and applicable to the same temporal scale.	Activity data specific to 1 year.
Composite Score	0.98	1.0	0.98		

[a] The “activity” is the amount of material (pollutant) used in a year and is directly measurable. The “factor” is the fraction of material used that is emitted to the atmosphere. The fraction is based on engineering calculations and is assumed to remain constant over the year.

TABLE 6.6-2

DARS SCORES: SOURCE TEST DATA

Attribute	Factor Score	Activity Score	Emissions Score	Factor Assumptions	Activity Assumptions
Measurement/Method	0.7 - 0.9	0.9 - 1.0	0.63 - 0.9	Lower score reflects a small number of tests at typical process rates; upper score represents numerous tests over a range of process loads.	Lower score reflects direct, intermittent measurement of activity; upper score reflects direct, continuous measurement of activity.
Source Specificity	1.0	1.0	1.0	Factor developed specifically for the intended source.	Activity data represent the emission process exactly.
Spatial Congruity	1.0	1.0	1.0	Factor developed for and specific to the given spatial scale (one process).	Activity data developed for and specific to the inventory area (one process).
Temporal Congruity	0.7 - 0.9	0.7 - 0.9	0.49 - 0.81	Lower score reflects factor developed for a shorter time period with moderate to low temporal variability; upper score reflects factor derived from an average of numerous tests during the year.	Lower score reflects activity data representative of short period of time with low to moderate temporal variability; upper score reflects activity data measured numerous times during the year.
Composite Score	0.85 - 0.95	0.90 - 0.98	0.78 - 0.93		

TABLE 6.6-3

DARS SCORES: SOURCE-SPECIFIC EMISSION FACTOR DATA[a]

Attribute	Factor Score	Activity Score	Emissions Score	Factor Assumptions	Activity Assumptions
Measurement/Method	1.0	0.9 - 1.0	0.9 -1.0	Continuous or near-continuous measurement of pollutant.	Lower scores reflect direct, intermittent measurement of activity; upper scores reflect direct, continuous measurement of activity.
Source Specificity	0.8	1.0	0.8	Factor developed for a similar category; low variability.	Activity data represent the emission process exactly.
Spatial Congruity	0.9	1.0	0.9	Factor developed from a process of similar size; low variability.	Activity data developed for and specific to the inventory area (one process).
Temporal Congruity	1.0	0.7 - 0.9	0.7 - 0.9	Factor developed for and applicable to a period of 1 year.	Lower score reflects activity data representative of short period of time with low to moderate temporal variability; upper score reflects activity data measured numerous times during the year.
Composite Score	0.93	0.90 - 0.98	0.83 - 0.90		

[a] Assumes emission factor was developed from an identical or similar facility and is of high quality.

TABLE 6.6-4

DARS SCORES: ENGINEERING CALCULATIONS

Attribute	Factor Score	Activity Score	Emissions Score	Factor Assumptions	Activity Assumptions
Measurement/Method	1.0	0.9 - 1.0	0.9 - 1.0	Continuous or near continuous measurement of activity; data capture >90%.	Lower scores reflect direct, intermittent measurement of activity; upper scores reflect direct, continuous measurement of activity.
Source Specificity	0.5 - 0.7	0.5 - 0.7	0.25 - 0.49	Factor developed for a somewhat similar process.	Activity data are somewhat correlated with emission process.
Spatial Congruity	0.9 - 1.0	1.0	1.0	Factor developed for a similar spatial scale (one process).	Activity data developed for and specific to the inventory area (one process).
Temporal Congruity	0.9 - 1.0	0.9 - 1.0	0.81 - 1.0	Factor derived from a nonspecific temporal scale.	Activity data measured for a similar period of time.
Composite Score	0.83 - 0.93	0.83 - 0.93	0.68 - 0.86		

7

DATA CODING PROCEDURES

This section describes the methods and codes available for characterizing emission sources at semiconductor manufacturing facilities. Consistent categorization and coding will result in greater uniformity among inventories. In addition, the procedures described here will assist the reader who is preparing data for input to the Aerometric Information Retrieval System (AIRS) or a similar database management system. The use of the Source Classification Codes (SCCs) provided in Table 6.7-1 is recommended for describing various semiconductor manufacturing operations. Refer to the Clearinghouse for Inventories and Emission Factors (CHIEF) help desk (919-541-1000) or internet address: *www.epa.gov/ttn/chief* for these codes and any additional codes that may be added to describe semiconductor manufacturing operations.

7.1 SOURCE CLASSIFICATION CODES

SCCs for various processes occurring at semiconductor manufacturing facilities are presented in Table 6.7-1. These include the following processes:

- Cleaning Processes (wet chemical);
- Cleaning Processes (plasma);
- Photoresist Operations;
- CVD Operations;
- Etching Processes (wet chemical); and
- Etching Processes (plasma).

TABLE 6.7-1

SOURCE CLASSIFICATION CODES FOR SEMICONDUCTOR MANUFACTURING PROCESSES

Source Description	Process Description	SCC	Units
Integrated Circuit Manufacturing	General	3-13-065-00	1000 Wafers
Cleaning Processes	Wet Chemical	3-13-065-01	Gallons Solution Consumed (Specify Aqueous Solution)
	Plasma Process	3-13-065-02	1000 Cubic Feet (Specific Gas Used)
Photoresist Operations	General	3-13-065-05	Tons Photoresist
Chemical Vapor Deposition	General	3-13-065-10	1000 Cubic Feet (Specify Gas Used)
Diffusion Process	Deposition Operation	3-13-065-20	1000 Cubic Feet (Specify Gas Used)
Etching Process	Wet Chemical	3-13-065-30	Gallons Solution Consumed (Specify Aqueous Solution)
	Plasma/Reactive Ion	3-13-065-31	1000 Cubic Feet (Specify Gas Used)

7.2 AIRS CONTROL DEVICE CODES

Control device codes that may be applicable to semiconductor manufacturing operations are presented in Table 6.7-2. These should be used to enter the type of applicable emission control device into the AIRS Facility Subsystem (AFS). The “099" control code may be used for miscellaneous control devices that do not have a unique identification code.

TABLE 6.7-2

AIRS CONTROL DEVICE CODES FOR SEMICONDUCTOR MANUFACTURING

Control Device	Code
Wet Scrubber - High Efficiency	1
Wet Scrubber - Medium Efficiency	2
Wet Scrubber - Low Efficiency	3
Direct Flame Afterburner	21
Direct Flame Afterburner with Heat Exchanger	22
Catalytic Afterburner	19
Catalytic Afterburner with Heat Exchanger	20
Miscellaneous Control Device	99

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8

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APPENDIX A

EXAMPLE DATA COLLECTION FORMS AND INSTRUCTIONS - SEMICONDUCTOR MANUFACTURING

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EXAMPLE DATA COLLECTION FORMS INSTRUCTIONS - SEMICONDUCTOR MANUFACTURING FACILITIES

1. These forms may be used as a worksheet to aid the plant engineer in collecting the information necessary to calculate emissions from semiconductor manufacturing facilities. The information requested on the forms relate to the methods (described in Sections 3, 4, and 5) for quantifying emissions. These forms may also be used by the regulatory agency to assist in areawide inventory preparation.

2. If the information requested is unknown, write "unknown" in the blank. If the information requested does not apply to a particular unit or process, write "NA" in the blank.

3. If you want to modify the form to better serve your needs, an electronic copy of the form may be obtained through the EIIP on the Clearinghouse for Inventories and Emission Factors (CHIEF) web site (www.epa.gov/ttn/chief/).

4. Collect all Material Safety Data Sheets (MSDSs) for all materials containing potential air contaminants that are used at the facility.

5. The plant engineer should maintain all material usage information and MSDSs in a reference file.

6. The completed forms should be maintained in a reference file by the plant engineer with other supporting documentation.

EXAMPLE DATA COLLECTION FORM

FORM A: GENERAL INFORMATION

Business Name:

SIC Code:

SCC:

SCC Description:

Location

County:
City:
State:

Plant Geographical Coordinates

Latitude:
Longitude:
UTM Zone:

Date of Initial Operation:

Equipment Type (Check one or more and complete corresponding forms)

[ ] Solvent Stations {Forms B1, C1, D - F}

[ ] Wet Chemical Stations {Forms B2, C2, D - F}

[ ] Coating/Solvent Application {Forms B3, C3, D - F}

[ ] Gaseous Operations {Forms B4, C4, D - F}

Contact Name:

Title:

Telephone Number:

EXAMPLE DATA COLLECTION FORM

FORM B1: SOURCE INFORMATION - Solvent Stations

Location:

Unit Description	Number of Units	Surface Area (ft^2)	Manufacturer	Date Installed	Date Modified
Solvent Station Hoods					

Operating Schedule

Hours/Day:

Days/Week:

Weeks/Year:

Typical % of Total Annual Usage:

Dec-Feb %

Mar-May %

Jun-Aug %

Sep-Nov %

Raw Material Used:

Material Name and Code	Constituents	Mass %	Annual Usage (gallons)	Reclaim (gallons)

EXAMPLE DATA COLLECTION FORM

FORM B2: SOURCE INFORMATION - Wet Chemical Stations

Location:

Unit Description	Number of Units	Surface Area (ft^2)	Manufacturer	Date Installed	Date Modified
Wet Chemical Station Hoods					

Operating Schedule

Hours/Day:

Days/Week:

Weeks/Year:

Typical % of Total Annual Usage:

Dec-Feb %

Mar-May %

Jun-Aug %

Sep-Nov %

Raw Material Used:

Material Name and Code	Constituents	Mass %	Annual Usage (gallons)	Reclaim (gallons)

EXAMPLE DATA COLLECTION FORM

FORM B3: SOURCE INFORMATION - Coating/Solvent Application

Location:

Unit Description	Number of Units	Manufacturer	Date Installed	Date Modified
Photoresist Developer Negative				
Photoresist Maskant Applicator Negative				
Photoresist Developer Positive				
Photoresist Maskant Applicator Positive				
Polyimide Applicator				
Polymer Resin Applicator				
Solvent/Solvent Mixture Applicator				
Spin-On Dopant/Glass Applicator				
Other: (Describe)				

Operating Schedule

Hours/Day: ________________

Days/Week: ________________

Weeks/Year: ________________

Typical % of Total Annual Usage:

Dec-Feb ________________ %

Mar-May ________________ %

Jun-Aug ________________ %

Sep-Nov ________________ %

EXAMPLE DATA COLLECTION FORM

FORM B3: SOURCE INFORMATION - Coating/Solvent Application (cont.)

Raw Material Used:

Material Name and Code	Constituents	Mass %	Annual Usage (gallons)	Reclaim (gallons)

EXAMPLE DATA COLLECTION FORM

FORM B4: SOURCE INFORMATION - Gaseous Operations

Location:

Unit Description	Number of Units	Manufacturer	Date Installed	Date Modified
Chemical Vapor Deposition, Atmospheric				
Chemical Vapor Deposition, Low Pressure				
Diffusion Furnace Chambers				
Ion Implementation Chambers				
Plasma Ashing Chambers				
Plasma/Ion Etch Chambers				
Siliconizing Reactors				
Sputtering Chambers				
Other: (Describe)				

Operating Schedule

Hours/Day: ____________

Days/Week: ____________

Weeks/Year: ____________

Typical % of Total Annual Usage:

Dec-Feb ____________ %

Mar-May ____________ %

Jun-Aug ____________ %

Sep-Nov ____________ %

EXAMPLE DATA COLLECTION FORM

FORM B4: SOURCE INFORMATION - Gaseous Operations (cont.)

Raw Material Used:

Material Name and Code	Constituents	Mass %	Annual Usage (cubic feet)	Reclaim (cubic feet)

EXAMPLE DATA COLLECTION FORM

FORM C1: CONTROL DEVICE INFORMATION - Solvent Stations

Location:

Unit Description	Device Type	Device Number	% Flow	Pollutant Controlled	Control Efficiency	Manufacturer	Date Installed	Date Modified	Hours/Day	Days/Week	Weeks/ Year
Solvent Station Hoods	1)										
	2)										
	3)										
	4)										

EXAMPLE DATA COLLECTION FORM

FORM C2: CONTROL DEVICE INFORMATION - Wet Chemical Stations

Location:

Unit Description	Device Type	Device Number	% Flow	Pollutant Controlled	Control Efficiency	Manufacturer	Date Installed	Date Modified	Hours/ Days	Days/ Weeks	Weeks/Year
Wet Chemical Station Hoods	1)										
	2)										
	3)										
	4)										

EXAMPLE DATA COLLECTION FORM

FORM C3: CONTROL DEVICE INFORMATION - Coating/Solvent Application Equipment

Location:

Unit Description	Device Type	Device Number	% Flow	Pollutant Controlled	Control Efficiency	Manufacturer	Date Installed	Date Modified	Hours/Day	Days/Week	Weeks/Year
Photoresist Developer Negative	1)										
	2)										
	3)										
	4)										
Photoresist Maskant Applicator Negative	1)										
	2)										
	3)										
	4)										
Photoresist Developer Positive	1)										
	2)										
	3)										
	4)										
Photoresist Maskant Applicator Positive	1)										
	2)										
	3)										
	4)										
Polyimide Applicator	1)										
	2)										
	3)										
	4)										

EXAMPLE DATA COLLECTION FORM

FORM C3: CONTROL DEVICE INFORMATION - Coating/Solvent Application Equipment (cont.)

Location:

Unit Description	Device Type	Device Number	% Flow	Pollutant Controlled	Control Efficiency	Manufacturer	Date Installed	Date Modified	Hours/Day	Days/Week	Weeks/Year
Polymer Resin Applicator, other	1)										
	2)										
	3)										
	4)										
Solvent/Solvent Mixture Applicator	1)										
	2)										
	3)										
	4)										
Spin-On Dopant/Glass Applicator	1)										
	2)										
	3)										
	4)										
Other: (Describe)	1)										
	2)										
	3)										
	4)										

EXAMPLE DATA COLLECTION FORM

FORM C4: CONTROL DEVICE INFORMATION - Gaseous Operations

Location:

Unit Description	Device Type	Device Number	% Flow	Pollutant Controlled	Control Efficiency	Manufacturer	Date Installed	Date Modified	Hours/Day	Days/Week	Weeks/Year
Chemical Vapor Deposition, Atmospheric	1)										
	2)										
	3)										
	4)										
Chemical Vapor Deposition, Low Pressure	1)										
	2)										
	3)										
	4)										
Diffusion Furnace Chambers	1)										
	2)										
	3)										
	4)										
Ion Implantation Chambers	1)										
	2)										
	3)										
	4)										
Plasma Ashing Chambers	1)										
	2)										
	3)										
	4)										

EXAMPLE DATA COLLECTION FORM

FORM C4: CONTROL DEVICE INFORMATION - Gaseous Operations (cont.)

Location:

Unit Description	Device Type	Device Number	% Flow	Pollutant Controlled	Control Efficiency	Manufacturer	Date Installed	Date Modified	Hours/Day	Days/Week	Weeks/Year
Plasma/Ion Etch Chambers	1)										
	2)										
	3)										
	4)										
Siliconizing Reactors	1)										
	2)										
	3)										
	4)										
Sputtering Chambers	1)										
	2)										
	3)										
	4)										
Other: (Describe)	1)										
	2)										
	3)										
	4)										

EXAMPLE DATA COLLECTION FORM

Form D: Stack Information (if applicable)

Stack ID:

Unit ID

Stack (Release) Height (ft):

Stack Diameter (inch)

Stack Gas Temperature (^{o}F):

Stack Gas Velocity (ft/sec):

Stack Gas Flow Rate (dscf/hr):

Source(s) Linked to this Stack:

EXAMPLE DATA COLLECTION FORM

FORM E: Material Data Forms (to be completed for each material used)

Manufacturer Name:

Material Description or Brand Name and Number:

Typical Units (Check one):

[ ] Gallons [ ] Pounds [ ] Cubic Feet [ ] Other ____________

Density: _____________ lb/gal or _____________ lb/ft^3

Volatile Organic Compound (VOC) Content: _____________ lb/gal or
_____________ wt % VOC in the material

Solids Content: ________ wt % solids in the material

True Vapor Pressure @ 70°F: ________ psia

Boiling Point: ________ °F

Antoine's Coefficients:
A __________________ B _______________
C __________________ Ref _______________

Molecular Weight: __________________ lb/lb-mole

Fuels: Heat Content	Btu usage/unit
__________________	______

EXAMPLE DATA COLLECTION FORM

FORM E: Material Data Forms (to be completed for each material used) (cont.)

Component Name	CAS#[a]	Wt % in Material	ppmv in Material

[a] CAS# = Chemical Abstract Service number.

EXAMPLE DATA COLLECTION FORM

FORM F: Emission Results

Pollutant	Emission Estimation Method	Emissions Value	Units of Emissions	Emission Factor	Emission Factor Units	Comments

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