United States Environmental Office of Air Quality Planning and Standards Research Triangle Park, NC 27711 February 2001



National Emission Standards for
Hazardous Air Pollutants
(NESHAP) for Source Category:
Manufacture of Semiconductors
-- Background Information for
Proposed Standards



National Emission Standards for Hazardous Air Pollutants (NESHAP) for Source Category: Manufacture of Semiconductors -Background Information for Proposed Standards

Emission Standards Division

U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711

February 2001

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ENVIRONMENTAL PROTECTION AGENCY

NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS (NESHAP) FOR SOURCE CATEGORY: MANUFACTURE OF SEMICONDUCTORS -BACKGROUND INFORMATION FOR PROPOSED STANDARDS

- The standards regulate organic hazardous air pollutant (HAP) emissions from the manufacture of semiconductors.
 Only those semiconductor manufacturing facilities that are part of major sources under section 112(d) of the Clean Air Act (Act) will be regulated.
- 2. For additional information contact:

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SEMICONDUCTOR MANUFACTURING NESHAP

BACKGROUND INFORMATION DOCUMENT

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1.0 INTRODUCTION

1.1 OVERVIEW

Section 112 of the Clean Air Act as amended in 1990 (CAA) requires that the United States Environmental Protection Agency (EPA) establish emission standards for categories of sources of hazardous air pollutants (HAP). National emission standards for hazardous air pollutants (NESHAP) for major sources of HAP are based on maximum achievable control technology (MACT), with a minimum level of control as defined in section 112(d). The CAA defines a major source as:

...any stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit, in the aggregate, 10 tons per year or more of any hazardous air pollutant or 25 tons per year of any combination of hazardous air pollutants.

On July 16, 1992, the initial list of categories of major sources that will be regulated under section 112 was published in the Federal Register (57 FR 31576). "Semiconductor Manufacturing" was included in the list as a category of major sources. The semiconductor manufacturing NESHAP project will

establish standards for semiconductor manufacturing facilities that are major sources.

The purpose of this document is to summarize the background information gathered during the development of the semiconductor manufacturing NESHAP.

1.2 PROJECT HISTORY

1.2.1 <u>Background</u>

On March 7, 1996, a meeting was held between the EPA and the Semiconductor Industry Association (SIA) to obtain feedback on a draft presumptive MACT (P-MACT) document that had been prepared by the EPA based on preliminary information gathered on the semiconductor industry. Subsequent to that meeting and meetings with State and local officials, the P-MACT document was revised into a draft Technical Information Document (TID). The TID, supplemented with additional, more recent information collected, and analyses of this information, served as the origin of this Background Information Document (BID). Several other meetings have been held in the interim with State and local agencies, Regional Offices of the EPA, and semiconductor industry representatives to gather and discuss specific information relevant to the determination of MACT.

1.2.2 Data Gathering

The Act requires that minimum control levels (MACT floors) be established for each category or subcategory regulated under section 112. These floors, discussed in more detail in Chapter 4.0 of this document, were based on an analysis of the level of control existing in a category prior to NESHAP regulation (i.e., at the baseline). In order to

obtain information to evaluate this baseline level of control, several approaches were considered, including:

- C Use of existing State regulations;
- C Use of discussions with State regulators;
- C Use of site visit reports of several semiconductor manufacturing facilities;
- C Use of national databases; and
- C Use of industry-developed questionnaires sent to semiconductor manufacturers.

After evaluating the options, it was determined that each one could provide unique and valuable information relevant to the regulatory development process, and the decision was made by the EPA to use them all.

Most of the information and data presented in this document is a result of input from the various partners affected by potential MACT development for the semiconductor manufacturing industry. The EPA collected process and emissions information on the semiconductor manufacturing source category from the industry and State regulatory agencies. The EPA specifically obtained input to identify major sources, examine concerns regarding area sources, determine the P-MACT level of control, gather permit information, and solicit comments on existing and new source MACT. This input was provided by representatives of the SIA; EPA Regions I, II, III, and IX; and the states of California, Oregon, Maryland, Vermont, Arizona, and Texas.

Information about the semiconductor manufacturing process, industry characteristics, HAP emissions, and emission controls was gathered from the SIA, Toxic Release Inventory (TRI) data, State files, existing literature, and site visits

to semiconductor manufacturing facilities. This information has been used to characterize the industry and to identify what data are needed to propose and establish a formal MACT. The information gathered to date is discussed below.

1.2.3 Participating Companies

The following companies and facilities (excluding those that have requested anonymity) have elected to participate by providing information on various activities that are conducted within a semiconductor facility. Much of the information pertaining to process and emission control descriptions in this document has been received from these companies.

AMD, Austin, TX	Motorola, Chandler, AZ
Delco, Kokomo, IN	Motorola, Mesa, AZ
IBM, East Fishkill, NY	Motorola, Phoenix, AZ
Intel, Ocotillo, AZ	Raytheon-TI, Dallas, TX
Intel, Rio Rancho, NM	Texas Instruments, Dallas, TX
Micron, Boise, ID	Triquint Semiconductor, Dallas, TX
Motorola, Austin, TX	VLSI, San Antonio, TX
Motorola, Austin-Oak Hill, TX	

1.2.4 Emissions and Control Data

The emissions and control information for the semiconductor manufacturing source category is summarized in chapter 3.0 of this document. Because of the rapid and frequent process modifications made by the semiconductor manufacturing industry, the specific point sources, HAP species emitted, magnitude of emissions, and methods of control described in this document are subject to change.

However, Chapter 3 presents the most recent information available to the EPA.

1.3 DEFINITIONS

Throughout the regulatory development process, it is essential that terminology is clearly defined and both the EPA and industry use these terms consistently. Lack of clarity in the meaning of crucial regulatory and industry-specific terms may lead to ambiguity in the final rule and confusion in its implementation. Appendix A contains definitions of words and phrases used in this document and are provided in order to avoid such problems.

2.0 SEMICONDUCTOR MANUFACTURING INDUSTRY CHARACTERIZATION AND EMISSIONS

2.1 INTRODUCTION

A semiconductor is a material with electrical conductivity between that of a conductor and an insulator; its electrical characteristics can be manipulated to behave like either depending on how the materials and circuitry inlayed in the wafer are configured and processed. Silicon has traditionally been the substrate used to manufacture semiconductors, although other materials are being developed for the semiconductor substrate, such as gallium arsenide (GaAs) and other valence III-V compounds. Materials similar to GaAs have several advantages over silicon, such as increased electron mobility as well as semi-insulating properties.

The operation of an integrated circuit depends on the ability to control the movement of charged carriers through an electrical pathway (circuit) constructed on or just below the surface of a semiconducting material. The circuit is fabricated by introducing impurities (dopants) in stringently controlled concentrations in precisely defined areas of the semiconducting material (substrate). The basic manufacturing process for semiconductors involves three stages: crystal growing, wafer fabrication, and assembly.

During the crystal growing stage, crystalline wafers of silicon or other specific semiconducting materials are manufactured for use as substrates in integrated circuit fabrication. In wafer fabrication, a group of chips are created on the wafer through a series of pattern-forming processes. Finally, during the assembly stage, the finished chips are separated, tested, and packaged for later use in various products.

2.1.1 <u>End Products</u>

The semiconductor manufacturing industry, a subset of the electronics manufacturing industry, produces integrated circuits or "chips." Integrated circuits combine the functions of discrete electronic devices in a miniature device that can perform complicated electronic functions in a fraction of a second. The electronics manufacturing industry produces devices such as computers, appliances, radios, CD players, and other finished goods that incorporate these integrated circuits.

Although semiconductors account for only a small portion of electronics/computer industry sales, semiconductors are crucial to all electronic products and to the U.S. economy. Semiconductors are used in computers, consumer electronic products, telecommunication equipment, industrial machinery, transportation equipment, and military hardware. Typical functions of semiconductors in these products include information processing, display purposes, power handling, data storage, signal conditioning, and conversion between light and electrical energy sources. According to the EPA's Design for the Environment (DfE) initiative, computers are the principal end use of semiconductors, constituting 40 percent of the market in 1992.

2.2 INDUSTRY CHARACTERIZATION

2.2.1 <u>Source Category Description</u>

Semiconductor manufacturing is classified under Standard Industrial Classification (SIC) code 3674 (North American Industry Classification System (NAICS) Code 334413). This SIC code includes any operation performed in the manufacture of semiconductor or related solid state devices. Examples of semiconductor or related solid state devices include semiconductor diodes, semiconductor stacks, rectifiers, integrated circuits, transistors, solar cells, and light sensing and emitting devices. SIC code 3674 includes all processing from crystal growth through circuit separation, encapsulation, and testing.

According to U.S. Census Bureau information,¹ there are approximately 1,099 facilities classified under the Standard Industrial Classification (SIC) code 3674 (semiconductors and related devices). Studies conducted by the SIA in 2000 and 2001 indicate that about 127 of these facilities are actually engaged in the manufacture of semiconductors. Table 2-1 list those semiconductor manufacturing facilities that have reported under the Toxic Release Inventory System.

2.2.2 <u>Semiconductor Market Characterization</u>

The U.S. global market share of semiconductors, semiconductor processing equipment, and computer systems fell between 1980 to 1991, but has grown since 1992.² In 1996 global sales of semiconductors was \$144.4 billion.³ The dynamics of the market also means that these industries are sensitive to global activities. In late 1998, global economic markets waned, slowing the demand, growth, and production of integrated circuits.

2.3 SEMICONDUCTOR MANUFACTURING PROCESSES

There are many steps within the design, development, and manufacture of an integrated circuit. Depending on its complexity, the logic network on which the semiconductor is based can take many months to design. To manufacture this design, the logic network must be translated into a series of electronic

TRIS Facility ID Number	Company	City	State	SIC Code
04084GTPRDROUTE	Control Devices Inc.	Standish	ME	3264
46904DLCLC1800E	Delco Electronics	Kokomo	IN	3469
24019TTLCT7635P	ITT Night Vision	Roanoke	VA	3671
87109GNRLT6816W	General Tech. Corp.	Albuquerque	NM	3672
85281LTTNS1215S	Litton Electro-Optic	Tempe	AZ	3672
94088DVNCD915DE	Advanced Micro Devices	Sunnyvale	CA	3674
78741DVNCD5204A	Advanced Micro Devices Inc.	Austin	TX	3674
19090SPRGL3900W	Allegro Microsystems	Willow Grove	PA	3674
01613SPRGL115NO	Allegro Microsystems	Worcester	MA	3674
83201MRCNM2300B	American Microsystems Inc.	Pocatello	ID	3674
75041SLCNM2613I	American Silicon Prods.	Garland	TX	3674
02908MRCNS15CLA	American Silicon Prods. Inc.	Providence	RI	3674
94089PRFRM610EW	Analog Devices	Sunnyvale	CA	3674
01887NLGDV804WO	Analog Devices Inc.	Wilmington	MA	3674
01821MBLSL4SUBU	ASE Americas Inc.	Billerica	МА	3674
80906HNYWL1150E	Atmel Corp.	Colorado Springs	CO	3674
85706BRRBR6730S	Burr-Brown Corp.	Tucson	AZ	3674
02818CHRRY2000S	Cherry Semiconductor Corp.	East Greenwich	RI	3674
03051CHMRC16FLA	Chomerks Div.	Hudson	NH	3674
32819TTMCR9333S	Cirent Semiconductor	Orlando	FL	3674
16130GTCRPRD2RO	Component Intertechnologies	Hadley	PA	3674
83642CMPTR499EC	Computrol Inc.	Meridian	ID	3674

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a (cont.)

TRIS Facility ID Number	Company	City	State	SIC Code
27713CRRSR2810M	Cree Research Inc.	Durham	NC	3674
45177CRYST180EM	Crysteco Inc.	Wilmington	ОН	3674
55425CYPRS2401E	Cypress Semiconductor	Bloomington	MN	3674
78664CYPRS17CYP	Cypress Semiconductor Inc	Round Rock	ТХ	3674
75244DLLSS4350B	Dallas Semiconductor Corp.	Dallas	ТХ	3674
01749DGTLQ75REE	Digital Equipment Corp.	Hudson	MA	3674
20110DMNNS9600G	Dominion Semiconductor	Manassas	VA	3674
74354GLPCH200BJ	Eagle-Picher Tech.	Miami	ОК	3674
14652STMNK1669L	Eastman Kodak	Rochester	NY	3674
10710LCTRN21GRA	Electronic Devices Inc.	Yonkers	NY	3674
64063TTTCH777NB	Fabtech Inc.	Lees Summit	МО	3674
84088NTNLS3333W	Fairchild Semiconductor	West Jordan	UT	3674
04106NTNLS333WE	Fairchild Semiconductor Corp.	South Portland	ME	3674
85034FLPCH3701E	Flip Chip Tech.	Phoenix	AZ	3674
97030FJTSM21015	Fujitsu Microelectronics Inc.	Gresham	OR	3674
11590GNRLN172SP	General Semiconductor Inc.	Westbury	NY	3674
01810GRMNMHAVER	Germanium Power Devices Corp.	Andover	МА	3674
19403CMMDR950RI	GMT Microelectronics	Norristown	PA	3674
32905HRRSCPALMB	Harris Semiconductor	Palm Bay	FL	3674

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a (cont.)

TRIS Facility ID Number	Company	City	State	SIC Code
95131HWLTT350WT	Hewlett-Packard Co.	San Jose	CA	3674
75063HTCHS6431L	Hitachi Semiconductor	Irving	ТХ	3674
75081HNYWL830EA	Honeywell Inc.	Richardson	ТХ	3674
92658HGHSR500SU	Hughes Aircraft Co.	Newport Beach	CA	3674
75034HTSNN1000H	Hutson Ind. Inc.	Frisco	ТХ	3674
05452BM 1000R	IBM	Essex Junction	VT	3674
11716LCDTD105WI	ILC Data Device Corp.	Bohemia	NY	3674
93905NTGRT1566M	Integrated Device Tech.	Salinas	CA	3674
95134NTGRT2670S	Integrated Device Tech. Inc.	San Jose	CA	3674
85248NTLCR4500S	Intel Corp.	Chandler	AZ	3674
97124NTRGR3131N	Intergrated Device Tech. Inc.	Hillsboro	OR	3674
13039NTLCN63336	International Controls	Cicero	NY	3674
90245NTRNT233KA	International Rectifier	El Segundo	CA	3674
92390HXFTM41915	International Rectifier	Temecula	CA	3674
92123KYCRM8611B	Kyocera America Inc.	San Diego	CA	3674
95035LNRTC1630M	Linear Tech. Corp.	Milpitas	CA	3674
92641SLCNG11652	Linfinity Microelectronics	Garden Grove	CA	3674
97030LSLGC23400	LSI Logic Corp.	Gresham	OR	3674
18103TTMCR555UN	Lucent Techs. Inc.	Allentown	PA	3674
19612TTMCR2525N	Lucent Techs. Reading	Reading	PA	3674

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a (cont.)

TRIS Facility ID Number	Company	City	State	SIC Code
01803MCMNCSOUTH	M/A-com Inc.	Burlington	MA	3674
75238MRLWN10451	Marlow Ind. Inc.	Dallas	ТХ	3674
98373NTNLS11113	Matsushita Semiconductor Corp.	Puyallup	WA	3674
97005MXMNT14320	Maxim Integrated Prods.	Beaverton	OR	3674
85281MCRRL2434W	Medtronic/Micro-Rel	Tempe	AZ	3674
63376MNSNT501PE	MEMC Electronic Materials Inc.	O'Fallon	МО	3674
75090MMCST6416U	MEMC Southwest	Sherman	TX	3674
02172NTRDC580PL	Micro USPD Inc.	Watertown	MA	3674
85224MCRCH2355W	Microchip Tech. Inc.	Chandler	AZ	3674
83706MCRNT2805E	Micron Tech. Inc.	Boise	ID	3674
92704MCRSM2830S	Microsemi Corp.	Santa Ana	CA	3674
12533MCRS HUDSO	Micrus	Hopewell Junction	NY	3674
27704MTSBSTHREE	Mitsubishi Semiconductor	Durham	NC	3674
97302MTSBS3990F	Mitsubishi Silicon America	Salem	OR	3674
80027MKQNT1450I	MKE - Quantum Components	Louisville	СО	3674
78721MTRLN3501E	Motorola	Austin	TX	3674
78735MTRLN6501W	Motorola Inc.	Austin	TX	3674
85202MTRLN2200W	Motorola Inc.	Mesa	AZ	3674
92718WSTRN1BANT	Motorola Mos 10	Irvine	CA	3674
27709GMCRL3026C	Motorola Mos 15	Durham	NC	3674
85008MTRLN5005E	Motorola	Phoenix	AZ	3674
85224MTRLN1300N	Motorola-Chandler	Chandler	AZ	3674

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a (cont.)

TRIS Facility ID Number	Company	City	State	SIC Code
76017NTNLS1111W	National Semiconductor	Arlington	TX	3674
04106NTNLS5FODE	National Semiconductor Corp.	South Portland	ME	3674
95678NCLCT7501F	NEC Electronics Inc.	Roseville	CA	3674
44281HBRSS8711W	Ohio Brass Co.	Wadsworth	ОН	3674
75006PTKTC1215W	Optek Tech. Inc.	Carrollton	TX	3674
48167PTCLM47050	Optical Imaging Sys.	Northville	MI	3674
94089RBTSM1230B	Orbit Semiconductor	Sunnyvale	CA	3674
87113SGNTC9201P	Philips Electronics Corp.	Albuquerque	NM	3674
94086SGNTC811EA	Philips Semiconductors	Sunnyvale	CA	3674
75243RYTHN13510	Raytheon TI Systems	Dallas	TX	3674
80907NTDTC1575G	Rockwell Semiconductor Sys.	Colorado Springs	CO	3674
94086XRCRP411NP	Rohm Corp.	Sunnyvale	CA	3674
94086XRCRP740KI	Rohm Device USA	Sunnyvale	CA	3674
78754SMSNG12100	Samsung Austin Semiconductor	Austin	TX	3674
95050SNMNC2539S	Sanmina Corp.	Santa Clara	CA	3674
98682SHMRC4111N	SEH America Inc.	Vancouver	WA	3674
01803SMCNC1011N	Semicon Components Inc.	Burlington	MA	3674
92127NRTHR16350	SGS Thomson Microelectronics	San Diego	CA	3674
75006SGSTH1310E	SGS-Thomson Microelectronics	Carrollton	TX	3674
95060SLCNS2300D	Silicon Sys. Inc.	Santa Cruz	CA	3674
95054SLCNX2201L	Siliconix Inc.	Santa Clara	CA	3674

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a (cont.)

TRIS Facility ID Number	Company	City	State	SIC Code
87113SLMXN5031S	Silmax Inc.	Albuquerque	NM	3674
78245DVNCD8611M	Sony Semiconductor Co	San Antonio	TX	3674
91341SPCTR12500	Spectrolab Inc.	Sylmar	CA	3674
11788STNDR35MAR	Standard Microsystems Corp.	Hauppauge	NY	3674
85024SMTMS19801	Sumitomo Sitix of Phoenix Inc	Phoenix	AZ	3674
45039CNCNN537GR	Sumitomo Sitix Silicon Inc.	Maineville	ОН	3674
94088SPRTX1225B	Supertex Inc.	Sunnyvale	CA	3674
80916NCRMD1635A	Symbios Inc.	Colorado Springs	CO	3674
80525NCRMC2001D	Symbios Logic Inc.	Fort Collins	CO	3674
85283MTRLN7204S	Tempe Motorola	Tempe	AZ	3674
75080TWNST500WE	Texas Instruments	Richardson	TX	3674
75090TXSNS6400H	Texas Instruments Inc.	Sherman	TX	3674
95051KWSKW2400W	Unisil Corp.	Santa Clara	CA	3674
95051KWSKW2400W	Unitrode Corp.	Merrimack	NH	3674
93010VTSSS741CA	Vitesse Semiconductor Corp.	Camarillo	CA	3674
78251VLSTC9651W	VLSI Tech. Inc.	San Antonio	TX	3674
95131VLSTC1109M	VLSI Technology Inc.	San Jose	CA	3674
93291VLTGM8711W	Voltage Multipliers Inc.	Visalia	CA	3674
55425VTCNC2800E	VTC Inc.	Bloomington	MN	3674
97210WCKRS7200N	Wacker Siltronic Corp.	Portland	OR	3674
95035XCRNC851BU	Xicor Inc.	Milpitas	CA	3674

Table 2-1. Semiconductor Manufacturing Facilities Reporting Under the Toxic Release Inventory System^a (cont.)

TRIS Facility ID Number	Company	City	State	SIC Code
83651ZLGNC26011	Zilog Inc.	Nampa	ID	3674
94303VRNSS611HA	Varian Associates	Palo Alto	CA	3844

^a Source: SIA.

circuits which will become the individual layers of circuitry that comprises the finished semiconductor.

The integrated circuits are formed by passing wafers through many iterations of the specific manufacturing process steps. Beginning with a thin silicon wafer cut from an ingot 10 to 20 centimeters (4 to 8 inches) in diameter (larger diameter ingots and thinner wafers are currently under development), consecutive layers of complex circuitry are built up, one on top of the another, to produce the completed chip. These layers of circuitry are created using a complex series of manufacturing processes that are repeated many times.

The manufacturing process for semiconductors involves three basic stages: crystal growing, wafer fabrication, and assembly. During the crystal growing stage, crystalline wafers of silicon or other specific semiconducting materials are manufactured for use as the substrate. In wafer fabrication, a group of integrated circuits are created on the wafer through a series of pattern-forming processes. Most of the chemicals used in the semiconductor manufacturing process are used in this step. Finally, during the assembly stage, the finished chips are separated, tested, and packaged.

The individual processes involved in semiconductor manufacturing are described below.

2.3.1 Crystal Growing

Most silicon for use in semiconductor manufacturing is made from a pure polycrystalline metal. A common source is the extraction and refinement of trichlorosilane from ordinary sand. From this material a monocrystalline silicon is produced. A number of processes for crystal growth are available. The most common is the Teal and Little adaptation

of the Czochralski method. In this method, a polycrystalline silicon, surrounded by an inert gas, is melted in a fused silica container (or crucible). A single-monocrystalline silicon seed is then provided to initiate ingot growth by lowering this seed until it contacts the surface. The cooler temperature of the seed causes the formation of the silicon structure and is then slowly retracted, producing a singlecrystal ingot of silicon.⁴

From an electrical standpoint this pure silicon is worthless. The resultant form is an insulator because of the tightly bound electrons restricting electrical charge flow. The nature of this material is changed through the introduction of specific impurities which change the properties of the crystal in a known manner, preferentially creating P-Type or N-Type semiconductor material. The growth of crystals may also be referred to "epitaxial growth" (grown from a vapor). In either method of crystal growing, the crystalline material is "doped" to produce N-Type or P-Type semiconductor substrate ingots. These ingots may be layered in this manner such that a cross sectional view of the ingot would display alternating layers of "N" and "P" type properties.

The type ingot is then sawed into thin wafer discs. Each disc is ground flat and polished to mirror smoothness. Where a single N-Type crystal is prepared, the slice is heated in a chamber, silicon chloride gas is pumped in, and the gas decomposes to a monocrystalline silicon deposited on the surface. The gas generally carries a small amount of the P-Type impurity.

2.3.2 <u>Wafer Preparation</u>

Ingots are shaped into wafer form through a series of cutting and grinding steps, usually performed using diamondtipped tools. The ends of the silicon ingots are removed and individual wafers are cut. The wafers may then be polished using an aluminum oxide/glycerine solution to produce uniform flatness across the surface of the wafer in a process called lapping. This initial shaping of the wafer leaves imperfections in the surface and edge of the wafers that are subsequently 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. Other contaminants such as organics are removed in solvent cleaning steps.

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 away. In some cases, bare silicon wafers are cleaned using ultrasound techniques that involve the use of potassium chromate or other mild alkaline solutions. In the final wafer preparation step, the wafers are usually rinsed in deionized water and dried with compressed air or nitrogen.

2.3.3 <u>Oxidation</u>

Oxidation is an initial and sometimes second or third step in the fabrication of the semiconductor wafer. A film of silicon dioxide is formed on the exterior surface of the wafer

in this step. The process takes place in a temperature- and pressure-controlled vessel to control the reaction between the surface of the silicon wafer and an oxidant gas such as oxygen or water vapor. A thin layer of silicon dioxide is formed, which insulates and protects the wafer during subsequent processing. Dry oxidation may use chlorine (in the form of chlorine gas), anhydrous hydrochloric acid, or trichloroethylene. At this point, the wafer is thoroughly cleaned and is ready for the initial application materials.

2.3.4 Photolithography

Photolithography transfers multiple patterns to a semiconductor wafer by exposure and development of a photosensitive material (photoresist) placed on the wafer. Patterns with widths less than a micrometer $(3.9 \times 10^{-5} \text{ inch})$ can be transferred using a photomask over the thin layer of photoresist material on the wafer. The resist is typically spun onto the wafer and baked to remove any solvent remaining in the resist material. Next, the photomask, which is generally a glass emulsion plate with a circuit design made from a hard-surface material such as chromium or iron printed on it, is placed over the wafer. Light is projected through the voids in the photomask causing the exposed surfaces of the wafer to be "developed." The unexposed areas of the photoresist are then removed through a development process (alternatively, depending on the process and photoresist used, the exposed photoresist may be removed) leaving the circuit pattern traced on the wafer.

The following lithography techniques are commonly used; however, the demand for better techniques and the everexpanding capabilities of ICs pose increasing challenges for

lithographic technology. Though steps such as spin on glass and resist etchback techniques have been developed to allow smaller (0.35 micron) designs, additional development of new techniques such as chemical-mechanical polishing have also emerged.

There are two types of photoresists:

1. <u>Positive</u> photoresists are chemicals made more soluble through exposure to radiation. During the development step, the developer (like in film processing) removes the resist that was exposed.

2. <u>Negative</u> resist are chemicals that polymerize and stabilize upon exposure to radiation. During the subsequent development the developer removes the resist that was not exposed.

Three types of radiation are used in photolithography: optical, electron beam, and X-ray. Each type has relative advantages and costs, but optical ultraviolet (UV) applications predominate. Electron-beam systems result in greater resolution than optical systems and can apply a circuit pattern directly on the photoresist without the use of a photomask. Electron-beam systems are typically used to create the photomasks used in optical systems.

In an optical system, the photoresist is exposed to UV light through the photomask. The photoresist either polymerizes (hardens) when exposed to light (if a negative resist is used) or unpolymerizes (if a positive resist is used). After exposure, the wafer is developed in a solution (e.g., trichloroethane, chlorobenzene, etc.) that dissolves the unwanted resist and is then rinsed to remove excess developer solution. The majority of development processes are

liquid immersion or spray methods, but dry plasma methods are also used.

After photolithography, the resulting wafer has a silicon dioxide layer exposed for the circuit pattern, with the rest of the wafer being covered with the remaining photoresist coating. Since the prepared photoresist surface resists etchants, the wafer can now be washed with etching chemicals to cut windows in the exposed oxide layer.

2.3.5 <u>Etching</u>

Etching involves liquid acids or reactive gases which etch away exposed oxide areas to create dimensional patterns (windows) on the wafer surface. After the photoresist is developed, the wafer is placed in a solution that etches the exposed silicon dioxide layer but does not remove the resist, creating the circuit pattern in the silicon dioxide layer. This pattern forms areas in which dopants will be applied to provide the required electrical properties. Several etching processes are available. Wet (i.e., liquid) chemical etching uses acid solutions to etch the exposed layer of silicon dioxide at ambient or elevated temperatures. Hydrofluoric, sulfuric, and nitric acids and hydrogen peroxide are typically used. However, wet etching is less effective for etching multiple plasma-deposited layers, and dry etching techniques have been developed that overcome the limitations of wet etching techniques.

In the most commonly used dry etching technique, plasma etching, a plasma gas is formed by ionizing process gases under a vacuum. Although dry etching usually involves reactive halogenated gases, nonhalogenated gases may also be used. Chemicals used during the dry etching process include chlorine, hydrogen bromide, carbon tetrafluoride, sulfur

hexafluoride, trifluoromethane, fluorine, fluorocarbons, carbon tetrachloride, boron bichloride, hydrogen, oxygen, helium, and argon. Other dry etching techniques include sputter etching, ion milling, reactive etching, and reactive ion beam etching.

After etching, the remaining photoresist is removed using dry or liquid stripping compounds. The etched and stripped wafer is ready for the diffusion furnace where under high temperatures a dopant is introduced to the exposed windows. 2.3.6 <u>Doping</u>

Doping occurs when ions of dopant materials are electrically or thermally driven into exposed areas of a patterned wafer to create electrically positive or negative conductive regions (PN junctions). To create the desired electronic components (transistors, resistors, etc.), impurities (called dopants) are introduced into the silicon dioxide pattern on the wafer. Dopants are introduced into the silicon dioxide pattern on the wafer either by diffusion or by ion implantation processes.

In the diffusion process, vaporized metals diffuse into exposed regions of the wafer. Dopant atoms are introduced using either a dopant-containing vapor in high-temperature furnaces (400 - 1000EC) (750 - 1,800EF) or a dopant-oxide layer coated on the wafer. The most commonly used dopants include arsenic, boron, and phosphorus, while aluminum, antimony, beryllium, gallium, germanium, gold, magnesium, silicon, tellurium, and tin are also used.⁵ In the diffusion process, dopant atoms take the place of a small portion of the silicon atoms in the crystal structure. Boron, for example, is a P-type dopant. Where boron is implanted, the silicon becomes a P-type junction. When the diffusion depth is achieved the wafer is removed and the process stops.

The ion implantation process is a physical deposition process that provides greater control of the number and depth of dopant atoms than does the diffusion process (a chemical process). In the ion implantation process, dopant sources are ionized in a vacuum chamber at ambient temperature. The ionized particles are then accelerated to high velocities and imbedded into the wafer by an ion implanter. The strength of the ion implanter voltage determines the depth of dopant implantation and the dopant gas usage. Typical gases used in the ion implantation process include arsine, phosphine, and boron trifluoride.

2.3.7 <u>Layering</u>

Layering covers the wafer with material that acts as a conductor (such as aluminum), semiconductor (such as silicon), or insulator (such as silicon dioxide). Prior to layering, the wafer is cleaned using the same techniques as those used in oxidation and doping. The primary layering methods available include deposition, metalization, and dielectric and polysilicon film deposition.

2.3.7.1 <u>Deposition</u>. Deposition processes may be used to apply additional layers of silicon, silicon dioxide, or other materials to the wafer. Deposition processes typically employ epitaxial growth, in which the substrate wafer acts as a seed crystal for the new layer. Dopants may be added to provide special electrical properties. Two techniques used for epitaxial growth are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE), with CVD being more common.

During CVD, materials are vaporized in a high-temperature reactant chamber furnace to produce a thin layer on the wafer.

Materials that may be used during CVD include silane, silicon tetrachloride, ammonia, nitrous oxide, tungsten hexafluoride, arsine, phosphine, and diborane.⁶ Another gaseous deposition technique is low-pressure CVD, which uses elevated-temperature vacuum chambers that may use nitrogen and/or silane, arsine, tetraethylorthosilicate, dichlorosilane, ammonia, hydrogen fluoride, and nitrous oxide.

In MBE, silicon and one or more dopants are evaporated and transported to the substrate at high velocity in a vacuum. This process is typically performed at lower temperatures than CVD. After a layer is applied, the wafer may undergo the steps previously described to impart additional electrical properties and circuits to the wafer.

2.3.7.2 <u>Metalization</u>. Metalization deposits metal layers at the atomic level for contacts and interconnections through condensation on the wafer surface. Metalization techniques include evaporation and sputtering and employ similar photolithography techniques as discussed above.

The evaporation method uses high temperatures to vaporize a metal that condenses on the wafer surface. Metals used in metalization include aluminum, platinum, titanium, nickel, chromium, silver, copper, tungsten, gold, and germanium. Evaporation methods include electron-beam evaporation of pure metal, resistance heating evaporation, and inductive heating evaporation. Argon gas is also used in some operations.

In the sputtering process, ionized gas atoms (e.g., argon) remove atoms from a target metal. These metal atoms deposit on the wafer to form a layer. Metals used in sputtering include titanium, platinum, gold, molybdenum, tungsten, nickel, and cobalt. Any unnecessary metals from this process may be removed by solvents or acid solutions.

2.3.7.3 <u>Dielectric and Polysilicon Films</u>. Dielectric and polysilicon films are deposited onto the wafer to provide conducting regions within the device, electrical insulation between metals, and protection from the environment. The most widely deposited films are polycrystalline silicon, silicon dioxide, and silicon nitride. Doping elements such as arsenic, phosphorus, and boron also may be added using this process. Oxygen may be added to polysilicon films to act as a semi-insulating material used for passivating the surface.

After the final layering, the wafer is rinsed in deionized water, a glass like material is applied to protect the wafer from contamination, the bottom of the wafer is mechanically ground, and a thin layer of gold is then plated to the bottom of the wafer.

2.3.8 <u>Cleaning</u>

Cleaning of wafers, tools and equipment, and other general items occurs throughout wafer fabrication. HAP materials are used for cleaning, including hydrochloric acid and methanol. Alcohol compounds may be used for cleaning chips in the final assembly process.

2.3.9 Assembly and Test

2.3.9.1 <u>Assembly</u>. Assembly involves a series of steps from cutting the individual chips from the wafer to the final packaging. The steps include: die cutting, die attach, postsolder cleaning, wire bonding, and encapsulation. In die cutting, the individual chips (or die) are separated from the wafer through laser or diamond impregnated saw. The chip is then mounted onto a metal frame (e.g., lead) through a soldering process or through use of an epoxy. Solvent blends or terpenes are used to conduct the post soldering cleaning or

defluxing. The next step is installing wire bonding (pins), which provides the connections from the metalized parts of the chip to the leads of the package or frame. In the encapsulation step, an airtight package made of plastic or epoxy resin seals the package. Ceramic caps are used for some applications.

2.3.9.2 <u>Testing</u>. The individual devices are tested on automatic electromechanical handling equipment by computers that apply static electrical tests and some dynamic electrical tests. Units that pass are marked and packaged.

2.3.10 Ancillary Processes

Ancillary processes in the semiconductor manufacturing industry include process cooling water, de-ionized water, room air conditioning, waste treatment, chemical storage and transport, process piping, and in some cases standby electrical generation equipment. De-ionized water production, either onsite or provided through a vendor, is the largest consumption of water and energy usage of all the ancillary activities at a fabrication facility.

2.4 HAP USAGE AND EMISSIONS

The physical and chemical processing steps discussed in Section 2.3 occur at four process operation areas: solvent stations, wet chemical stations, coating application stations, and gaseous operation stations. These process operation areas are discussed in Section 2.4.4. A variety of pollutants may be emitted at these stations. These include acid fumes and organic solvent emissions from cleaning, rinsing, resist drying, developing, and resist stripping; hydrogen chloride emissions from etching; and other various emissions from spent etching solutions, spent acid baths, and spent solvents.⁷ In

addition to process related emissions, air emissions may also result from onsite treatment of industrial wastewater. 2.4.1 HAP Usage.

According to information provided by the SIA,⁸ 29 different HAP materials were reported as being used by the 20 facilities participating in the study. Ion bed regeneration for deionized water production exhibited the highest HAP usage. Lithography operations represent the largest use of HAP in wafer production, with wet etch representing the second largest HAP usage. These HAP materials are predominantly organic. The other processes with significant HAP usage, consisting primarily of acids and organic solvents, are diffusion, epitaxy, and some cleaning operations. Inorganics other than acids comprise only a small percentage of the HAP usage. As reported by the SIA, five chemicals comprised 95 percent of the total HAP usage: hydrochloric acid (HCl), hydrofluoric acid (HF), glycol ethers, methanol, and xylene.9 Of this 95 percent, 76 percent were acids (87 percent HCl), 23 percent were organics (32 percent xylene, 29 percent methanol, 22 percent glycol ethers), and 1 percent were inorganics (metals, hydrides, chlorine). The SIA study showed that eleven chemicals represented over 90 percent of reported HAP emissions.¹⁰

A subsequent SIA study¹¹ showed that the following 10 chemicals comprised approximately 93.8 percent of all controlled HAPs emitted, with methanol being the most predominant:

> ethylbenzene ethylene glycol methylene chloride

methanol
glycol ethers	perchloroethylene
hydrochloric acid	trichloroethylene
hydrofluoric acid	xylene

The remaining chemicals reported included the following:

acetaldehyde	ethyl benzene
acrylonitrile	ethylene glycol
antimony	ethylene oxide
arsenic compounds	formaldehyde
arsine	hydrazine
benzene	hydroquinone
beryllium compounds	lead
1,3-butadiene	methylene chloride
cadmium compounds	methyl ethyl ketone
carbon tetrachloride	naphthalene
catechol	nickel
chlorine	phenol
chloroform	phosphine/phosphorous
chromium	silane
cresols	tetrachloroethylene
cyanide	toluene
diethanolamine	1,2,4-trichlorobenzene
1,4-dioxane	

According to the SIA, HAP usage in the semiconductor industry is declining due to regulatory, worker safety, and cost pressures, and the trend is likely to continue.¹² Many HAP materials used in semiconductor manufacture have been replaced by HAP-free materials.

2.4.2 <u>Number of Exhaust Streams</u>

As a result of the sterility required of clean rooms for most semiconductor manufacturing processes, facilities typically have few air exhaust streams. These air exhaust streams are characteristically high-volume, low-velocity streams resulting in dilute pollutant concentrations. In general, the entire fabrication plant consists of two different classes of HAP emissions, acids and organics. These two classes of emissions are separated for treatment by the appropriate control device. Each tool or station within a semiconductor fabrication facility must meet certain OSHA standards for worker protection. In general, each tool has an exhaust system which may include point of use (POU) devices tied to a series of plenums that are then directed to control equipment.

2.4.3 <u>Uncontrolled Emissions</u>

According to a facility by facility HAP emission accounting conducted by the SIA, the industry also has uncontrolled emission points within the semiconductor manufacturing process. Approximately 65.1 megagrams per year (Mg/yr) (71.6 tons per year (tpy)) of uncontrolled emissions were identified by the 11 facilities that participated in the study. Of this amount, 54.0 Mg/yr (59.3 tpy) (or about 83 percent of the uncontrolled emissions) are associated with cleaning, photoresist formulation (mixing), ceramic layering activities, and other activities.

2.4.4 Process Operation Areas and Emissions

The physical and chemical processing areas associated with semiconductor manufacturing can be classified into four

general types: solvent stations, wet chemical stations, coating application stations, and gaseous operation stations.

2.4.4.1 <u>Solvent Stations</u>. Solvent station emissions are subject to control under the Halogenated Solvent Cleaning NESHAP. Cleaning materials (primarily organic solvents) are used to prepare and clean wafers for subsequent processing or for parts cleaning.

Solvent stations are batch and in-line machines. The solvent removes water-insoluble soils such as waxes and may be used to dry material by the displacement of moisture with the solvent, which is subsequently evaporated. Both batch and inline machines are designed to use solvent either at room temperature (i.e., cold cleaners) or solvent vapor (i.e., vapor cleaners). Solvent stations may be operated at elevated temperatures with manual or ultrasonic agitation.

Typical solvents and cleaning agents include acetone, deionized water, xylene, glycol ethers, isopropyl alcohol, hydrogen peroxide and sulfuric acid.¹³ Organic solvent cleaners use halogenated and nonhalogenated solvents or solvent blends. The vast majority of halogenated solvent use is in vapor cleaning, both batch and in-line. Cold cleaners typically use mineral spirits, Stoddard solvent, and alcohols. Very little halogenated solvent use has been identified in batch cold cleaning.¹⁴ Traditional semiconductor cleaning processes often use chlorofluorocarbons (CFC) and chlorinated hydrocarbons (e.g., trichloroethylene), and trichlorotrifluoroethane (CFC-113 or Freon™) may be used to dry the components after rinsing.¹⁵ CFC have been used in vapor degreasing of vacuum system components by using a mixture of CFC-113 and methyl alcohol. General solvent types used for wafer wax removal include hydrocarbon-based or

terpene-based solvents, amines, acids, and mixtures of these and other agents. The most commonly used cleaning solution in semiconductor manufacturing includes a combination of hydrogen peroxide and sulphuric acid.

2.4.4.2 <u>Wet Chemical Stations</u>. Wet chemical stations are used to clean wafers, remove photoresist, and etch patterns into the wafer's silicon or metal surfaces. Materials used during the wet etching process may include acids (sulfuric, phosphoric, nitric, hydrofluoric, and hydrochloric), ethylene glycol, hydrogen peroxide, hydroxide solutions, and solutions of ammonium, ferric, or potassium compounds.¹⁶ Hydrofluoric acid is used to wet etch silicon. Phosphoric acid is used to wet etch aluminum, which may be deposited on the wafer during the evaporation or sputtering step. Etching stations that use acids are vented through hoods that are typically connected to a wet scrubber for control.

2.4.4.3 <u>Photoresist Application, Developing, and</u> <u>Stripping Stations</u>. This general step in the semiconductor process may be classified as a coating operation. Processes in this industry that can be classified as coating operations include the photoresist application, spin-on glass, and application of adhesives and resins. Developer stations and rinses may also be included here. Emissions occur through evaporation or atomization. Typically, once the photoresist material has been spun onto the wafer, solvents in the photoresist are evaporated by baking the wafer at low temperature.

During the lithography step, developers are used that may also result in emission losses. Negative photoresist developers may include xylene or Stoddard solvent, and

positive photoresist developers include potassium hydroxide, sodium hydroxide, and tetramethyl ammonium hydroxide (TMAH).

Although mentioned in this section, some photolithography steps may be associated with the general group of solvent stations or wet chemical stations. Organic solvents are commonly used as liquid strippers to remove the photoresist from wafers containing metals. Liquid photoresist strippers for non-metalized surfaces commonly include hydrogen peroxide, sulfuric acid and ammonium persulfate, and sulfuric and nitric acid blends. Strippers for metallic surfaces most commonly contain an organic acid and chlorinated hydrocarbons. Other solutions include chromic and sulfuric acid mixtures, aqueous amines, and solvents.

2.4.4.4 <u>Gaseous Operation Stations</u>. Many of the processes at semiconductor manufacturing facilities occur in gaseous environments. Gaseous environments may be used for photoresist stripping, cleaning, doping, etching, or layering operations. Specific processes include CVD, plasma-enhanced CVD, diffusion furnace chambers, ion implantation chambers, plasma etching chambers, plasma/ion etching chambers, and siliconizing reactors. Dry stripping photoresist may utilize oxygen plasma, which requires no chemical processing, and thus results in no HAP emissions.

Emission sources from the doping process include excess dopant gases and contaminated carrier gases.

Oxidation and deposition processes may use HAP gases, such as chlorine or phosphine, at elevated temperatures. Such processes are commonly controlled by wet scrubbers due to the formation of acids from the thermal breakdown of chlorinecontaining compounds. In dry chemical stations, perfluorocarbon (PFC) gases such as hexafluoroethane are used for etching wafers and cleaning reactors in plasma processes. The PFC gases in the reactor chamber form fluorine species, including hydrofluoric acid and hydrogen fluoride. However, the conversion of PFC gases to hydrofluoric acid is incomplete, and a complete accounting of each fluorine species is difficult to obtain.

2.4.4.5 <u>Miscellaneous Operations</u>. Including the reference to ancillary operations such as process cooling water, laboratory operations, and deionized water chemical supply and storage, semiconductor production generates emissions from assembly and test wipe cleaning, equipment maintenance and assembly, and final mark and pack operations associated with packaging for distribution. Typically, these process contribute a small amount of air emissions as compared to the entire facility.

2.4.5 <u>HAP Materials and Waste Characterization in the</u> <u>Semiconductor Manufacturing Industry</u>

The following waste characterization is typical of the waste streams generated during the manufacture of semiconductors:

• Epitaxy - Acidic gaseous emissions are produced during the epitaxy process containing silane (SiH_4) and hydrogen chloride.

• Oxidation - Pyrolitic oxidation using TEOS produces gaseous emissions containing $Si(C_2H_5O)_4$ and oxygen. Chemical vapor deposition oxidation emits gaseous vapors containing silane, oxygen, and hydrogen.

• Photolithography - The photoresist coating stage involves resins and results in a solvent waste stream that

typically contains xylene. Developing and rinsing uses alkalis and acids resulting in liquid waste streams containing these materials.

• Etching - Oxide etching using hydrofluoric acid produces an acidic effluent containing metals. Nitric etching using sulfuric acid, ozone depleting substances, carbon tetrachloride and carbon tetraflouride produces a low pH effluent. Polysilicon etch produces a high pH rinse. Plasma etch produces a waste stream of metals, acids, and fluorides. Metal etch produces an effluent with a high metal content.

• Diffusion and Implant - The diffusion and implant stages produces a variety of waste depending on the type of dopants used. Gaseous emissions may include hydrogen fluoride, arsine, phosphine, and arsenic. Liquid wastes contain residual dopant and phosphorus oxychloride. Solid arsenic waste is associated with diffusion.

• Metalization - Sputtering and evaporation techniques produce solid waste mainly comprised of heavy metals.

• Passivation by Low Pressure Chemical Vapor Deposition - The process produces a gaseous waste stream containing silane and hydrogen chloride.

2.5 NATIONAL BASELINE EMISSIONS

The semiconductor manufacturing industry has a record of reducing HAP emissions. Table 2-2 presents the reduction in HAP emissions from all reporting semiconductor manufacturers from 1987 through 1994. Emission reductions are based on TRI data reported for SIC code 3674. Based on this data, aggregate HAP emissions fell from 2,426 Mg (2,668 tons) in 1987 to 579 Mg (636 tons) in 1994. Figure 2-1 shows the same

data normalized for the surface area of silicon used in the integrated circuit substrate.

The baseline emissions for this MACT category have been reduced over several years. The industry efforts directed at substitution, elimination, and end-of-pipe control applications have resulted in greatly reducing the number of major affected sources since the initial category listing. Based on information provided by the SIA, the baseline emission of major and co-located area sources is approximately 68 Mg/yr (75 tpy). The three primary HAP pollutants in the bseline are methanol at 25 Mg/yr (28 tpy), xylene at 15 Mg/yr (16 tpy), and perchlorethlylene at 19 Mg/yr (21 tpy).

HAP	1987	1988	1989	1990	1991	1992	1993	1994
1,1,1-Trichloroethane	2,027,269	2,724,521	2,541,609	2,401,186	1,596,634	1,135,257	339,952	92,487
1,2,4-Trichlorobenzene	49,550	62,973	73,918	19,323	4,762	4,522	6,519	10,100
Methylene Chloride	586,482	556,062	518,206	303,824	181,669	104,430	51,683	34,656
Ethylbenzene	25,000	21,980	34,570	11,600	10,640	8,810	1,475	1,815
Ethylene Glycol	1,500	5,360	10,459	3,967	2,316	3,326	12,004	33,849
Glycol Ethers	171,746	165,417	193,357	224,793	198,741	229,642	257,472	205,519
Hydrochloric Acid	188,445	174,420	208,153	206,142	113,969	112,995	95,625	101,792
Hydrofluoric Acid	65,411	93,954	60,193	80,420	81,126	56,683	63,692	48,963
Lead	295	186	1,026	184,631	1,569	760	750	770
Methanol	267,395	555,026	510,794	419,465	414,195	256,462	204,225	210,946
Methyl Ethyl Ketone	39,717	92,610	184,043	181,038	208,220	223,296	138,132	73,319
Phenol	42,506	205,245	71,205	35,069	5,924	1,511	2,795	1,850
Tetrachloroethylene	423,666	495,626	410,296	202,667	135,518	43,996	55,548	71,400
Toluene	37,072	32,369	78,176	48,900	56,550	89,728	84,292	86,726
Trichloroethylene	1,007,021	1,147,956	665,955	562,719	361,692	197,046	177,671	112,047
Xylene (Mixed Isomers)	403,352	481,519	646,437	482,843	456,100	350,680	312,898	186,607
Total	5,336,427	6,815,224	6,208,397	5,007,587	3,829,625	2,819,144	1,804,733	1,272,986

Table 2-2. HAP Emissions from Semiconductor Manufacturing as Reported to the Toxic Release Inventory (TRI), 1987-1994



Figure 2-1. TRI Reportable HAP Releases per Area of Silicon Substrate

2.6 REFERENCES

- U.S. Department of Commerce, Bureau of the Census. 1997 Economic Census, Comparative Statistics for United States, Manufacturing by Industry (4-digit SIC). Available at: http://www.census.gov.
- SIA. Chip Facts: World Market Sales and Shares for 1982-1995. http://www.semichips.org
- 3. SIA press release #32, October 29, 1997. Global Chip Market to Grow nearly 17% in 1998; Total Sales Should Exceed \$232 Billion in 2000. http://www.semichips.org
- 4. Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition. John Wiley and Sons, New York, 1997. Volume 21, page 1092.
- 5. Profile of the Electronics and Computer Industry. U.S. Environmental Protection Agency, Washington, D.C. Publication No. EPA/310-R-95-002. 1995.
- 6. Reference 5.
- 7. Reference 5.
- 8. SIA Report to EPA. November 1994.
- 9. Reference 8.
- 10. Reference 8.
- 11. SIA Major Source Survey Summary of results. Presented to EPA on November 26, 1996
- 12. Reference 11.
- 13. Reference 5.
- 14. National Emission Standards for Hazardous Air Pollutants: Halogenated Solvent Cleaning - Background Information Document. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 453/R-93-054. 1993.

- 15. Meier, G. Cleaning Solvent Substitution in Electronic Assemblies. Second International Congress on Environmentally Conscious Manufacturing, August 29 -September 1, 1993. KCP-613-5279, prepared under Contract No. DE-76-DP00613. U.S. Department of Energy, Arlington, VA.
- 16. Reference 5.

3.0 EMISSION CONTROL TECHNIQUES

3.1 CONTROL OF HAP EMISSION SOURCES

Hazardous air pollutant control measures in the semiconductor manufacturing industry include add-on control devices and preventive measures. Add-on control devices include adsorbers, oxidizers, concentrators, and absorbers (wet scrubbers). In addition, point-of-use control devices can be used on individual process equipment. Preventive measures include product substitution and reformulation, work practice procedures, and equipment modifications.

3.2 ADD-ON CONTROL DEVICES

3.2.1 Adsorbers.

Adsorption is a process in which organics are selectively collected on the surface of a porous solid. Activated carbon is the adsorbent most often used for low organic gas concentrations because of its low cost and relative insensitivity to water vapor at relative humidities below about 50 percent. Other common adsorption media include silica- and alumina-based adsorbates. Because adsorption processes simply

separate the contaminant from the gas stream, adsorption processes must be used in conjunction with other unit operations to recover or destroy the pollutants. There are

two types of adsorption systems that can be used for removal of organic vapors from gas streams. These are nonregenerable and regenerable (fixed-bed systems). The use of nonregenerable adsorption systems on low concentration, high flow pollutant streams in the semiconductor manufacturing industry has not been reported.

3.2.2 <u>Oxidizers</u>

Oxidation is a thermal process that converts organic compounds to CO_2 and H_2O . Incineration is widely used for the destruction of a variety of organic vapors and is best suited to applications where the gas stream has a consistent flow rate and concentration.

In thermal oxidation, the organic process exhaust is heated to very high temperatures to oxidize the organic compounds in the gas phase. To save fuel, a heat exchanger (either regenerative or recuperative) is often used to recover the heat generated during incineration by preheating the inlet gas. Thermal oxidizers without heat recovery are not known to be used to control high flow, low concentration gas streams. This is due to the high rate of fuel consumption when compared to systems using heat recovery or catalysis.

Because silicon dioxide (SiO_2) is a product of the oxidation of some exhaust streams emitted by semiconductor manufacturing, and because SiO_2 causes catalyst plugging, catalytic oxidizers are rarely used to control organic emissions in semiconductor manufacturing.

Depending on the type of heat recovery unit, oxidizers are further classified as regenerative or recuperative. Regenerative oxidizers are discussed in Section 3.2.2.1, and recuperative oxidizers are discussed in Section 3.2.2.2.

3.2.2.1 <u>Regenerative</u>. Regenerative thermal oxidizers consist of a flame-based combustion chamber that connects two or three fixed beds containing inert (e.g., ceramic) packing. Incoming gas enters one of the beds where it is preheated. The heated gas flows into the combustion chamber, burns, and the hot flue gases flow through the packed beds which capture, store, and allow recovery of the heat generated during oxidation. The packed beds store the heat energy during one cycle and then release it as the beds preheat the incoming organic vapor-laden gas during the second cycle. Up to 95 percent of the energy in the flue gas can be recovered in this manner.¹

3.2.2.2 <u>Recuperative</u>. Recuperative oxidizers use shell and tube heat exchangers to transfer the heat generated by incineration to preheat the feed stream. Recuperative thermal oxidation has a much lower thermal efficiency and as a result, it is far less economical for low concentration streams, such as those found in the semiconductor manufacturing industry. Recuperative oxidizers are not known to be used in the semiconductor manufacturing industry.

3.2.3 <u>Concentrators</u>

Some semiconductor manufacturing facilities are installing rotary concentrator systems for control of organic HAP emissions.² Zeolite rotary concentrators followed by thermal oxidation are a typical example.

Rotary concentrators use a rotating wheel containing adsorbent material which is partially exposed to the influent waste gas stream. The wheel adsorbs the volatile pollutants in the influent stream and subsequently desorbs them using steam or heat. The desorbed stream is relatively rich in volatiles, and this lower-volume higher-concentration stream

is typically oxidized. One shortcoming of rotary concentrators in the semiconductor manufacturing industry is their lack of affinity for methanol, which is controlled at only 40-60 percent.³

3.2.4 <u>Absorbers</u>

Wet scrubbing is a process used by the semiconductor manufacturing industry to remove inorganic pollutants from air streams. In absorption-based scrubbing, one or more soluble components of the air stream are dissolved in a liquid. Typically, water is the liquid of choice reported by the SIA.⁵ The absorption equipment most commonly used for pollution control is the packed tower, in which a column filled with packing material provides a large surface area for thorough contact between the gaseous and liquid streams. Removal efficiencies depend on the specific pollutant-solvent combination, the type of absorber used, and the physical configuration of the scrubber and media interface. In general, absorbers have removal efficiencies of 90 percent or higher.

A wet scrubber may be used to control acetone and other water miscible VOC. The scrubber effluent containing water soluble chemicals is typically routed to a local wastewater treatment plant.

3.2.5 Point of Use

Non-acid inorganic HAP emissions produced at semiconductor manufacturing facilities include reactive gases and minute quantities of metals. The pyrophoric nature of reactive gases imposes certain safety requirements on gas handling. Because these gases tend to react with oxygen, the formation of oxygen particulates that collect in piping and pumps also create substantial maintenance problems. The

devices used to control non-acid inorganic reactive gases include thermal reaction chambers (burn boxes), non-thermal reaction chambers, or electrically-charged reaction chambers (dry scrubbers). Some facilities regularly vent reactive gases to central wet scrubbers and use control devices described above for emergency release of inorganic exhaust streams containing reactive gases such as phosphine.

In general, point-of-use (POU) control systems are designed for treating air emissions from the outlet of the manufacturing process to remove the compounds of interest and prevent them

from entering the main exhaust ductwork. Historically, POU control systems have been installed for reducing production downtime and for health and safety reasons. Recently, air emissions reductions have been another reason for using POU control systems; however, their use for this purpose does not allow for their recognition as part of the tool in establishing potential to emit. 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 later system type is the main criteria for inclusion of the POU as an integral part of the tool when determining PTE.

3.3 REFERENCES

- Zerbinia, R.A., J. Spivey, S. Agarwal, W. Sanford. Survey of Control Technologies for Low Concentration Organic Vapor Streams. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 456/R-95-003. May 1995. Pages 2-15.
- 2. SIA Major Source Survey Summary of Results. Presented to the EPA on November 26, 1996.
- 3. EPA/SIA/EIA Briefing. Durham, NC. December 11, 1996.
- 4. Reference 3.
- 5. Reference 3.

4.0 MACT FLOORS AND REGULATORY ALTERNATIVES

This chapter presents the maximum achievable control technology (MACT) floors for existing and new sources of hazardous air pollutant (HAP) emissions in the semiconductor manufacturing source category and describes the methodology used to determine the recommended floors. Regulatory alternatives more stringent than the floor are also discussed, but none is recommended.

The recommended MACT floor is based on the selection of oxidation as the reference control technology representative of the average emission limitation achieved by the best performing five existing sources for which data were available. In previous rulemakings, the EPA has recognized that an oxidizer can generally achieve 98 percent control when the concentration of pollutants in the exhaust stream is sufficiently high. When the pollutant concentration is low, performance efficiency of an oxidizer decreases and the EPA has established a maximum emission rate of 20 parts per million by volume (ppmv) as being equivalent to 98 percent control. Thus, for the semiconductor manufacturing source category, an emission reduction of 98 percent or a maximum emission rate of 20 ppmv was determined to be equivalent to the MACT floor reference control technology. Similarly, the

recommended reference technology for new sources (the "best of the best") is also oxidation.

The MACT floor analysis was based on data from facilities that were either major sources or would be major sources if not for the use of add-on control devices. The floor data includes stack test data for 17 process vent emission points from six "synthetic minor" sources. A synthetic minor source is a source that would be major but for the use of add-on control devices. In addition, engineering estimates were collected for 9 process vents at the only known major semiconductor manufacturing facility bringing the total number of vents considered to 26.

The 1990 Clean Air Act (CAA) requirements for the determination of MACT floors are discussed in Section 4.1. The general approach used to determine the MACT floors for the semiconductor manufacturing source category is discussed in Section 4.2. Section 4.3 presents the analysis of alternatives more stringent than the floor.

4.1 CLEAN AIR ACT REQUIREMENTS

For standards established under section 112(d) of the CAA, the minimum level of required control is defined as the "MACT floor." For new sources, emission standards "shall not be less stringent than the emission control that is achieved in practice by the best controlled similar source." For existing sources, the emissions standards must be at least as stringent as either "the average emission limitation achieved by the best performing 12 percent of the existing sources," or "the average emission limitation achieved by the best

performing five sources" for categories or subcategories with less than 30 sources.

4.1.1 Definition of "Average"

The minimum level of control defined under section 112(d) of the CAA (". . . the average emission limitation achieved by the best performing 12 percent of the existing sources. . ." and for a source category with fewer than 30 sources ". . . the average emission limitation achieved by the best performing five sources . . . ") is commonly referred to as the MACT floor. The term "average" is not defined in the CAA. In a Federal Register notice published on June 6, 1994 (59 FR 29196), the EPA announced its conclusion that Congress intended "average," as used in section 112(d)(3), to mean a measure of mean, median, mode, or some other measure of central tendency. The EPA concluded that it retains substantial discretion, within the statutory framework, to set MACT floors at appropriate levels, and that it construes the word "average" (as used in section 112(d)(3)) to authorize the EPA to use any reasonable method, in a particular factual context, of determining the central tendency of a data set.

In addition, the EPA stated it has discretion to use "best engineering judgement" in collecting and analyzing data relevant to a MACT floor determination and in assessing the data's comprehensiveness, accuracy, and variability, in order to determine which sources achieve the best emission reductions. The EPA also has discretion in determining the appropriate "average" in each source category (see 59 FR 29199). In this MACT floor analysis, the EPA chose a modal analysis to determine the most frequently used control technology reported by the best performing sources. An average of the level of control (removal efficiency) achieved

by these sources was not used in this analysis for the reasons discussed in Section C, below.

4.1.2 <u>Meaning of "Source"</u>

The CAA does not define "source." A source may be a facility, a kind of emission point, or a collection of emission points. For the process vent MACT floor analysis, a source was defined as an individual process vent. This approach was selected as being the most appropriate because it makes the best use of the available data. For example data were not available for all process vents at a facility, so the control level achieved by an entire facility could not be adequately described. However, data were available on a number of specific emission points for which emission testing was performed.

4.1.3 Meaning of "Best Performing" and "Best Controlled"

For the MACT floor analysis, performance was measured in terms of control device removal efficiency as determined through the use of recognized test methods. The "best performing" semiconductor manufacturing facilities were those with the highest removal efficiencies.

Section 112(d)(3) of the CAA requires that the basis of the MACT floor for new sources be "the emission control achieved in practice by the best controlled similar source." The facility with the highest removal efficiency was considered to be the best controlled source for this analysis.

4.2 DETERMINATION OF THE MACT FLOORS FOR EACH SOURCE TYPE

Based on data gathering efforts that included site visits, industry survey responses, and literature searches, four potential emission sources of HAP emissions were identified for the semiconductor manufacturing industry.

These sources were process vents, storage tanks, wastewater treatment, and equipment leaks. No controls were identified in use to control HAP emissions from storage tanks, wastewater treatment, or equipment leaks based on the information obtained from the data gathering efforts. Therefore, the MACT floor for these sources is no control.

The individual semiconductor manufacturing operations typically produce process vent emission streams that consist primarily of organic or inorganic compounds. At some facilities, the organic and inorganic process vent emission streams are segregated to facilitate control, while others combine them into one or more common exhaust streams. For purposes of the MACT floor analysis, all the data obtained for the 26 process vents were considered together. No distinction was made between organic, inorganic, or combined emission streams for the test data because the same level of control can be achieved whether the streams are segregated or combined.

Using the test report summaries for the 26 process vents, the removal efficiency was calculated from the inlet and outlet concentration values for each process vent emission The process vents were then ranked from highest to stream. lowest removal efficiency, as presented in Table 4-1. This ranking was performed to determine the most prevalent control technology, not to determine the average removal efficiency. This decision was made because the performance of control devices in the semiconductor manufacturing industry is affected by highly variable inlet conditions. The performance of those control devices varies in response to inlet conditions and is more erratic at lower inlet conditions. Any single control device will perform at peak efficiency on an

episodic basis under optimum conditions, but the removal efficiencies represented by these test results cannot necessarily be maintained under all operating conditions that are typical in the semiconductor manufacturing industry.

The MACT floor for process vents for existing sources was determined from the best performing five process vents from Table 1 rather than the average of the top 12 percent because less than 30 process vents are represented. Four of the top five best performing process vents used some form of thermal oxidation, and this control technology was considered to be representative of the MACT floor. Consistent with other previously promulgated NESHAP for process vents,¹ the level of

Table 4-1. Control Device Removal Efficiency for Semiconductor Manufacturing Facilities^a

Company	Location	Emission Point	Control Device ^b	Removal Efficiency (percent)
Motorola	Austin, TX	EPN E-AE-1	TO	98.8
Motorola	Phoenix, AZ	No. 4 at P Building	RC/TO	98.4
Intel	Ocotillo, AZ	Fab 12, SC-F-3	Scrubber	97.7
Motorola	Phoenix, AZ	not listed	RTO	97.1
Motorola	Phoenix, AZ	No. 3 at Building D	RC/TO	97.1
Motorola	Phoenix, AZ	P Building	RC/TO	96.7
Motorola	Mesa, AZ	MOS 21, SC-19-1	Scrubber	96.4
Motorola	Chandler, AZ	not listed	RTO	95.8
Motorola	Phoenix, AZ	C-36-P	Scrubber	95.7
Motorola	Mesa, AZ	MOS 21, SC-19-3	Scrubber	93.5

Table 4-1. Control Device Removal Efficiency for Semiconductor Manufacturing Facilities^a (cont.)

Company	Location	Emission Point	Control Device ^b	Removal Efficiency (percent)
Intel	Rio Rancho, NM	Fab 10.1.1f	Scrubber	93.3
Motorola	Phoenix, AZ	C-28-P	Scrubber	92.7
Motorola	Mesa, AZ	MOS 6, MOS 21, BP3	Carbon Adsorber	92.0
Motorola	Phoenix, AZ	COM-1	RC/TO	91.7
Intel	Rio Rancho, NM	Fab 9.1.3a	Scrubber	91.4
Intel	Rio Rancho, NM	Fab 10.1.1d	Scrubber	88.4
Intel	Rio Rancho, NM	Fab 10.1.1e	Scrubber	84.0
Kodak	Rochester, NY	Building 81- 81001	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81002	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81003	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81004	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81005	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81006	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81009	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81010	None	0.0 ^b
Kodak	Rochester, NY	Building 81- 81011	None	0.0 ^b

^a Source: Stack test results provided by the facilities.
^b RC/TO = rotary concentrator/thermal oxidizer
RTO = regenerative thermal oxidizer
^c Source: Engineering estimates provided by the facility.

control deemed to be generally achievable by a combustion control device is 98 percent removal efficiency. This value was selected as the MACT floor for process vents at existing semiconductor manufacturing facilities. Because the same considerations for low concentration, high flow exhaust streams apply equally to new sources and the best controlled source used a thermal oxidizer, this level of control was also selected as the new source MACT floor.

In order to account for the variability in the performance of control devices used in the semiconductor manufacturing industry, as well as the increased variability inherent in the test methods when analyzing the high flow, low concentration process vent emission streams typically controlled by these devices, the MACT floor includes an alternate format based on outlet concentration of HAP. This alternate format is intended to provide facilities with added flexibility to comply with the standard when the inlet concentration of the add-on control device drops below the point where optimum control efficiency can be achieved, and it would not be feasible to require optimum performance levels (expressed in terms of removal efficiency) to be met. То again be consistent with previous NESHAP that have specified a control level of 98 percent through the use of a combustion control device, the alternate format for the process vent MACT floor was selected to be a HAP concentration limit of 20 ppmv corrected to 3% oxygen.²

4.3 CONSIDERATION OF REGULATORY ALTERNATIVES ABOVE THE MACT FLOOR

4.3.1 Process Vents

For process vents, the MACT floor of 98 percent control was found to be the highest level of control achievable on a consistent basis. While control devices such as thermal oxidizers can be operated under certain conditions to achieve greater than 98 percent removal efficiency, this was not deemed achievable on a consistent basis for the varying emission streams present throughout the semiconductor manufacturing industry. Thus, no regulatory alternatives above the floor value of 98 percent control were identified that were expected to be technically feasible.

However, it is possible that a facility can achieve the 20 ppmv alternative emission limit without the use of add-on control devices. Such a facility could install add-on control devices to achieve an emission rate lower than the 20 ppmv alternative emission limit. Thus, this would represent a regulatory option more stringent than the MACT floor.

For control above the floor we examined what it would cost to further control the one major source in this source category. The Kodak facility currently contains nine emission streams from the semiconductor manufacturing process. Kodak has conducted an engineering study to determine the feasibility of upgrading their vent system to standards currently in place in the semiconductor industry and installing the appropriate control technology. The recent engineering study³ conducted by Kodak determined that their emission streams could be segregated into two inorganic streams for control with wet scrubbers, and two organic

streams for control with regenerative thermal oxidizers. The estimated cost of this project was \$2,734,100.

For the purposes of estimating the cost per ton of emission reduction of this above the floor option, it was assumed that the Kodak facility emitted the maximum amount (20 ppmv) under the alternate emission limit, and that this emission rate would be reduced to 5 ppmv after installation of the add-on controls. As detailed in Appendix B, this would lead to an emission reduction in excess of that achieved by the MACT floor alone of 27.7 tons/yr.

The emission rate used in this analysis is in excess of Kodak's actual HAP emissions of approximately 1 ton/yr, and is used only for the purpose of this analysis to determine the lowest cost per ton of emission reduction. We chose a higher emission rate in order to better analyze the benefits of control more stringent than the selected floor value. Under this scenario the resulting cost would then be \$98,700/ton of emission reduction. This value was considered to be unreasonable; therefore, requiring existing sources to install add-on control devices to achieve an emission limit less than the 20 ppmv alternative emission limit was rejected as an above the floor option for process vents.

4.3.2 <u>Storage Tanks</u>

The vast majority of storage tanks in the semiconductor manufacturing industry are the containers in which the chemicals are shipped. As these containers are small (less than 200 gallons) and portable, they do not lend themselves to venting to a control device. Because these containers are not

refilled on site, there are no filling losses and emissions are minimal. For these reasons, we identified no alternatives above the MACT floor of no control that would be technically or economically feasible.

4.3.3 <u>Wastewater</u>

We identified no wastewater HAP emission controls in use by the industry. Wastewater streams from the semiconductor manufacturing industry consist predominately of HCl. HCl does not readily volatilize, and is not readily emitted to the atmosphere. In addition, the amount of HAP contained in wastewater from the manufacture of semiconductors is very small, typically on the order of 3 to 4 ppmv. Due to these factors the potential for emissions is very small. We have required control of wastewater streams in past rules such as the HON. The HON, however, does not require control of HCl due to its low emission potential. Additionally, the HON determined that control of wastewater streams below 1,000 ppmv was not cost effective. As previously stated, semiconductor streams are well below this level. Therefore, we determined that control above the floor is not feasible.

4.3.4 Equipment Leaks

Nearly all semiconductor manufacturing operations are conducted in highly controlled clean room environments. As such, equipment leaks that could contaminate this environment cannot be tolerated and are immediately repaired. While the industry has no formal leak detection and repair (LDAR) programs in place, the procedures inherent in the industry control equipment leaks to the maximum extent possible. Consequently, no regulatory options, such as requiring a formal LDAR program, would result in any additional emission reduction.

4.3.5 Process Changes

Finally, we examined process changes that would reduce the amount of HAP used, and thus have the potential to reduce emissions from all four emission points. Specifically, we looked at requiring industry to increase the size of wafers used in the manufacture of integrated circuits. Industry studies indicate that going to the next larger size of wafer decreases a facility's HAP usage by about 20 to 30 percent. Typically, sizes used are 4, 6, and 8 inch wafers.

However, we determined that these process changes are not cost effective because an increase in wafer size requires replacing most of the equipment in a wafer fabrication facility. The one major source covered by these NESHAP would need to replace approximately \$150 million worth of equipment in order to reduce emissions by several hundred pounds. Additionally, the major source we examined is a small facility, and would not be able to accommodate the larger equipment necessary to handle a larger wafer size. Therefore, we determined that process changes would not be a cost effective or practical method for reducing HAP emissions.

4.4 References

- 6. See, e.g., 40 CFR 63, subpart G, §63.113(a)(2).
- 7. See, e.g., 40 CFR 63, subpart G, §63.114(a)(2); subpart U, §63.485(a); subpart CC, §63.(a)(2); subpart DD, and §63.693(f)(1)(i)(B).
- Kodak Building 81 South Upgrade Exhaust Systems Final Technical Report. Erdman Anthony Consulting Engineers, Rochester, New York. August 1999.

5.0 ENVIRONMENTAL, ENERGY, AND COST IMPACTS

5.1 INTRODUCTION

The purpose of this chapter is to present the estimated environmental, energy, and cost impacts related to implementing the MACT floor level of control for new and existing semiconductor manufacturing facilities. The MACT floor level of control was determined to be 98 percent control of HAP emissions from semiconductor manufacturing facilities. A maximum HAP emission rate of 20 ppmv was determined to be equivalent to 98 percent control.¹ The impacts presented here are based on achieving this equivalent emission rate.

5.2 NEW SOURCES

Based on studies performed by the SIA, which represents over 90 percent of the semiconductor manufacturing companies in the U.S., no new sources that would be classified as major sources² are expected to be built in the next five years. While growth is expected in the industry, including the construction of new semiconductor manufacturing facilities, these facilities are expected to follow the prevailing industry trend of reducing emissions below major source levels. Emissions will be reduced through pollutionprevention measures, as well as installing add-on control devices. The new facilities are also expected to incorporate

these control requirements into their title V permits, making the control requirements federally enforceable. Thus, no environmental, energy, or cost impacts are expected for new semiconductor manufacturing facilities.

5.3 EXISTING SOURCES

As presented in Chapter 2.0, there are approximately 127 facilities that are actually engaged in the manufacture of semiconductors. Of the potentially affected facilities, only one facility (Eastman Kodak located in Rochester, NY) is expected to be a major source at the time of promulgation of the NESHAP. The existing source impacts were based on the Kodak facility.

5.3.1 Environmental Impacts

The Kodak facility currently meets the MACT floor level of control by maintaining HAP emissions below the 20 ppmv limit. As such, the facility will not have to implement pollution prevention measures or install add-on control devices as a result of the promulgation of the rule, and no further emission reductions are anticipated. However, the rule will have the effect of limiting future emissions increases at the Kodak facility to the 20 ppmv limit. While the effect on reducing future emissions increases cannot be quantified, the rule will effectively limit HAP emissions to at or near their current levels.

Secondary environmental impacts are typically associated with increased energy usage related to either fuel consumption by an add-on control device (such as natural gas burned by an oxidizer) or increased electricity demand on power plants. Since no additional controls will be required at the Kodak facility, no secondary environmental impacts are expected.

5.3.2 <u>Energy Impacts</u>

Similar to secondary impacts, energy impacts are typically associated with fuel consumption by an add-on control device or increased electricity demand on power plants. Since no additional controls will be required at the Kodak facility, and monitoring provisions are not expected to increase energy consumption, no energy impacts are expected. 5.3.3 Cost Impacts

No control costs will be incurred by the Kodak facility for meeting the MACT floor level of control because the facility is currently achieving that level of control. However, the proposed rule will impose certain monitoring, recordkeeping, and reporting (MR&R) requirements that will consume labor hours of facility personnel. These labor requirements primarily result from monitoring parameters to assure compliance to the emission limit and generating the required reports.

We estimate the Kodak facility will incur a \$68,200 cost during the first three years to conduct all monitoring, inspection, reporting, and recordkeeping (MIRR) activities during the first three years after promulgation of the NESHAP. Other sources will not incur any costs from these proposed NESHAP. Because no capital costs will be incurred by the one major source the total cost of the proposed NESHAP will be \$68,200 in MIRR costs.

5.4 REFERENCES

- For a complete discussion of the MACT floor determination, see the following: Memorandum from Hendricks, D., EC/R Inc., to Schaefer, J., EPA:ESD. November 6, 2000. MACT Floor Recommendation for the Semiconductor Manufacturing Source Category.
- Section 112(a)(1) of the Clean Air Act defines a major source as a source that emits or has the potential to emit 10 tons/yr of any HAP or 25 tons/yr of an combination of HAP.
- 3. OMB 83-I Supporting Statement, "ICR for the Semiconductor Manufacturing Source Category." ICR Number 1952-01. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. February 2001.

APPENDIX A

DEFINITIONS
DEFINITION OF TERMS

Abatement or recovery device (add-on control device) means any equipment that reduces the quantity of pollutant that is emitted to the atmosphere. The device may destroy or secure the pollutant for subsequent recovery. Examples are oxidizers, carbon adsorbers, condensers, and scrubbers.

Assembly means the final step in the integrated circuit manufacturing process where the chip is mounted onto a metal frame, connected to the leads, and enclosed in a protective housing. Testing of the completed assembly is also included in this step.

Capture efficiency means the fraction (usually expressed as a percentage) of the pollutants generated by a process that is directed to an abatement or recovery device.

Chip (see integrated circuit)

Control device (see abatement or recovery device)

Control efficiency means one minus the fraction (usually expressed as a percentage) of the pollutants that are emitted from the control device compared to the pollutants entering the control device.

Destruction removal efficiency (DRE) (see control efficiency)

Die (see integrated circuit)

Doping means the introduction through electrical or chemical means of impurities into the silicon during crystal growing. Typical doping materials include arsenic, boron, and phosphorus. Doping provides extra electrons or places for electrons to go. The type of doping material determines the "N" or "P" type nature of the crystalline lattice.

Epitaxy means growing a layer of monocrystalline silicon from silicon vapor. The layer usually contains dopant gas to produce PN junctions, or to produce a more lightly doped layer of the same type as the substrate.

Etching means the use of liquid acids or reactive gases to remove exposed areas of the wafer silicon oxide layer and silicon substrate surface to produce dimensional windows. Film thickness means the thickness of the dry, cured coating on the substrate.

Hazardous air pollutant (HAP) means any of the compounds identified in Section 112(b) of the Clean Air Act.

Industrial Grade Integrated Circuit (IC) means an IC with a performance typically guaranteed over the temperature range of 0 to 70EC.

Integrated circuit means an electronic circuit containing transistors and perhaps diodes, resistors, and capacitors, along with the interconnecting electrical conductors processed and contained entirely within a single chip of silicon.

Layering means the application of successive layers of conductive or insulating material over the wafer surface.

Metalization means the deposition by means of evaporation or sputtering of metal layers on the circuit image to form contacts and interconnects. Metal applications include conductors such as gold, aluminum, copper, and tin.

Military Grade IC means an IC whose performance is typically guaranteed over the range of -55 to +125EC.

Oxidation means the process of chemically reacting oxygen or water vapor with the surface of a silicon wafer to form a thin layer of silicon dioxide.

Photolithography means the process by which a circuit image is transferred to a photoresist covered wafer. Photolithography includes the application and curing of the photoresist, the imaging process, and developing of the exposed photoresist.

Photomask means a transparent plate containing opaque areas used in photolithographic processes. The photomask contains the circuit image that is transferred to the photoresist layer during the imaging step.

Photoresist means a liquid plastic which hardens into a tough, acid resistant solid when exposed to ultraviolet light. Through the use of a photomask, the circuit image is transferred to the wafer. Semiconductor means a material with electrical properties between that of a conductor and an insulator. Also used to refer to integrated circuits in general.

Semiconductor manufacturing means the collection of semiconductor manufacturing process units used to manufacture p-type and n-type semiconductors or active solid state devices from a water substrate, including processing from crystal growth through circuit separation, encapsulation, and testing. Examples of semiconductor or related solid state devices include semiconductor diodes, semiconductor stacks, rectifiers, integrated circuits, and transistors.

Semiconductor manufacturing process unit means the collection of equipment used to carry out a discrete operation in the semiconductor manufacturing process. These operations include, but are not limited to, crystal growing; solvent stations used to prepare and clean materials for subsequent processing or for parts cleaning; wet chemical stations used for cleaning (other than solvent cleaning); photoresist application, developing, and stripping; etching; gaseous operation stations used for stripping, cleaning, doping, etching, and layering; separation; encapsulation; and testing. Research and development operations conducted at a semiconductor manufacturing facility are considered to be semiconductor manufacturing process units.

Tool means the equipment that is used individually or in concert in a wafer manipulation step (e.g., etching, photolithography) necessary to the manufacture of the integrated circuit.

Wafer means a thin piece of silicon material cut from a silicon ingot. The wafer provides the initial substrate from which the semiconductor chips are manufactured.

APPENDIX B

COST PER TON OF EMISSION REDUCTION CALCULATION FOR ABOVE THE FLOOR LEVEL OF CONTROL FOR PROCESS VENTS

Cost Per Ton of Emission Reduction Calculation for Installing Add-on Controls to Semiconductor Manufacturing Process Vents

Assumptions

- 1. Before control emission stream contains 20 ppmv HAP.
- 2. After control emission stream contains 5 ppmv HAP.
- 3. The HAP in the emission stream is xylene.
- 4. The total flow rate to be controlled is 50,160 cfm (see Footnote 3 in the text of the memorandum).
- 5. The facility operates continually for 16 hours per day, 5 days per week, 52 weeks per year.
- 6. Cost of controls is \$2,734,100 (see Footnote 3).

Emission Reduction Calculation

Emission reduction = 20 ppmv - 5 ppmv = 15 ppmv

Converting to mass:

(50,160 ft³/min)(15 ft³ xylene/10⁶ ft³)(60 min/hr)(16 hr/day)(5 days/wk)(52 wk/yr) = 187,799 ft³ xylene/yr

Assuming ideal gas behavior and standard conditions, then $359 \text{ ft}^3 = 1 \text{ lb-mole}$

(187,799 ft³ xylene/yr)/(359 ft³ xylene/lb-mole xylene) = 523.1 lb-mole xylene/yr

Since 1 lb-mole xylene = 106 lbs xylene,

(523.1 lb-mole xylene/yr)(106 lbs xylene/lb-mole xylene) = 55,449 lb xylene/yr = 27.7 tons xylene/yr

Cost Per Ton of Emission Reduction Calculation

Cost per ton of emission reduction equals the cost of implementing the control measure divided by the annual emission reduction resulting from the control measure:

Cost = \$2,734,100/27.7 tons = \$98,700/ton of emission reduction

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 ABSTRACT A draft rule for the regulation of hazardous air pollutants (HAP) from semiconductor manufacturing operations is being proposed under the authority of Section 112(d) of the Clean Air Act. This document contains comments the background information used to develop the draft rule. 				
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