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EMISSION SCENARIO DOCUMENT ON PHOTORESIST USE IN SEMICONDUCTOR MANUFACTURING

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Series on Emission Scenario Documents No. 9

EMISSION SCENARIO DOCUMENT ON PHOTORESIST USE IN SEMICONDUCTOR MANUFACTURING

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**OECD Environment Directorate,
Environment, Health and Safety Division**

**2 rue André-Pascal
75775 Paris Cedex 16
France**

Fax: (33-1) 44 30 61 80

E-mail: ehscont@oecd.org

EXPLANATORY NOTES

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns, and potential release pathways of chemicals used in the semiconductor manufacturing industry. The document presents standard approaches for estimating environmental releases of and occupational exposures to additives and components used in photoresist formulations.

This ESD supersedes the *OECD Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing* [OECD, 2004a]. The 2004 ESD has been revised and expanded to incorporate additional information relevant to the occupational exposure methods, as well as to meet the U.S. Environmental Protection Agency (EPA)'s revised quality standards for generic scenarios [CEB, 2006].

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, the ESD can be further updated to reflect changes in the industry and new information available, and extended to cover the industry area in countries other than the lead (the United States). Users of the document are encouraged to submit comments, corrections, updates, and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org) and EPA (EPA contact: Nhan Nguyen, nguyen.nhan@epa.gov). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. Submitted information will also be made available to users within the OECD web site (www.oecd.org/env/riskassessment).

How to use this document

This document may be used to provide conservative, screening-level estimates of environmental releases of and occupational exposures to *nonvolatile* chemical components contained in photoresist formulations used in semiconductor manufacturing. Such estimates might result in release and exposure amounts that are likely to be higher, or at least higher than average, than amounts that might actually occur in real world practice.

The users of this ESD should consider how the information contained in the document applies to the specific scenario being assessed. Where specific information is available, it should be used in lieu of the defaults presented in this document, as appropriate. All input values (default or industry-specific) and the estimated results should be critically reviewed to assure their validity and appropriateness.

Coverage and Methodology

The approaches described in this ESD are based on readily available data[1], as well as consultation with industry representatives on photoresist use within semiconductor manufacturing processes in the United States. EPA developed this ESD using relevant data and information on photoresist use within the semiconductor manufacturing industry, including process descriptions, operating information, chemicals used, wastes generated, waste treatment, worker activities, and exposure information. EPA supplemented the data collected with standard models[2] to develop the environmental release and occupational exposure estimating approaches presented in this ESD.

The primary sources of information cited in this ESD include the U.S. Semiconductor Industry Association (SIA) and other individuals having working experience within the semiconductor manufacturing industry, Kirk-Othmer Encyclopedia of Technology, the U.S. Census Bureau's County Business Patterns (CBP) and Annual Survey of Manufacturers (ASM), and the International Semiconductor Environmental Safety and Health Conference (ISESH). EPA also incorporated data gathered during a site visit to a semiconductor manufacturing facility. Section 8 lists additional information on the sources investigated and the references cited in this document. Appendix C lists additional relevant sources of information.

The information in this document is based on U.S. data. Certain aspects of the photoresist use/semiconductor manufacturing process may differ in other countries; therefore, alternate assumptions and parameters may be necessary in some applications of this emission scenario.

This ESD includes methods for estimating environmental releases of and associated occupational exposures to *nonvolatile* chemical components contained in photoresist formulations, as used in the manufacture of semiconductor products (Industry Category 4 – electrical/electronic industry). Photoresists are polymer-based liquids that are applied in layers to silicon wafer surfaces to create a pattern and comprise of photo-active compounds, resins, stabilizers, polymerization inhibitors, viscosity control agents, dyes, plasticizers, and solvents. This ESD may be applied to any of these additives except solvent compounds.

The approaches presented in this ESD apply only to facilities that manufacture semiconductors. This ESD does not cover the manufacture of chemical raw materials or other additives used in photoresists, nor does it cover the formulation/manufacture of the photoresist product. Below is an illustration of the scope of this ESD within the context of the life cycle of the chemical of interest.

This ESD presents methods for estimating the following releases and exposures to photoresist components used to manufacture semiconductors and associated facility operating parameters:

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[1] Please refer to Section 8 for a list of the specific references used in developing this ESD.

[2] EPA has developed a series of "standard" models for use in performing conservative release and exposure assessments in the absence of chemical- or industry-specific data. Several of these standard models are described in Appendix B to this ESD.

- Number of sites in the United States that use photoresists containing the chemical of interest to manufacture semiconductors, and the duration of these activities;
- Release amount from transport container residue (via container cleaning or direct disposal of empty containers);
- Release amount from excess dispensed photoresist that does not adhere to the wafer surface;
- Release amount from routine equipment cleaning and maintenance;
- Release amount from developing the wafer;
- Release amount from etching and stripping the wafer;
- Number of workers that may come into contact with photoresists;
- Dermal exposures during transport container change-out;
- Dermal exposures during container cleaning and/or disposal;
- Dermal exposures during waste/excess photoresist handling;
- Dermal exposures during waste solvent (developer, stripping) handling; and
- Dermal exposures during equipment cleaning and maintenance activities.

To provide background information on the entire process, additional descriptions of other semiconductor manufacturing steps that do not involve photoresist releases or exposures, such as thin film deposition or doping, are provided in Appendix D. There are no releases of or exposures to the nonsolvent components of the photoresists during these steps. Because photoresist chemicals are not used in other semiconductor manufacturing operations, releases and exposures to chemicals during these operations have not been evaluated in this document.

How this document was developed

The U.S. Environmental Protection Agency (EPA), with support from Eastern Research Group, Inc. (ERG), has revised this Emission Scenario Document (ESD) on photoresist use in semiconductor manufacturing. The scope of the ESD is designed to serve the needs of both EPA and OECD programs. The Chemical Engineering Branch (CEB) of EPA’s Office of Pollution Prevention and Toxics (OPPT) is responsible for preparing occupational exposure and environmental release assessments of chemicals for a variety of programs under the Toxic Substances Control Act (TSCA). While OECD ESDs traditionally focus on the potential releases of chemicals from industrial processes, this document also describes approaches for estimating potential occupational exposures to photoresist chemicals. The occupational exposure methods are included so that the ESD may be used to fully support EPA's chemical review programs.

A draft of the 2004 ESD was initially submitted by EPA and circulated among the OECD member countries in December 2002. Comments were received from Canada, Germany, and the Netherlands. Data supplied on the German industry on facility throughput, days of operation, release estimates, and corresponding media of release were reviewed and found to be comparable to the industry in the United States. These data are noted throughout the ESD.

The comments from these countries and additional input from U.S. industry were incorporated into this document, which was published by OECD in June 2004. It should be noted that, because occupational exposures are not typically included in OECD ESDs, the approaches for assessing occupational exposures may not have been included in the review process for most OECD member countries.

Since publication of the ESD in 2004, EPA has solicited additional input and comment from U.S. industry representatives, specifically on the methods and assumptions used to estimate occupational exposures to photoresist chemicals within the semiconductor manufacturing process. Section 5.0 of this ESD has been significantly expanded to incorporate this new information.

A draft of revised ESD was circulated to the Task Force in July 2007 and approved at the meeting of the Task Force in December 2007.

This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology of the OECD.

TABLE OF CONTENTS

EXPLANATORY NOTES 7

Purpose and background 7
How to use this document 7
Coverage and Methodology 8
How this document was developed 9

1 INDUSTRY SUMMARY AND BACKGROUND 16

1.1 Introduction to Semiconductors 16
1.2 Manufacture of Semiconductors 16
1.3 Overview of Photoresists 18
1.4 Overview of the Semiconductor Manufacturing Industry 19

2 PROCESS DESCRIPTION 20

2.1 Photolithography 22
2.1.1 Photoresist Application 25
2.1.2 Soft Bake, Imaging, and Hard Bake of the Photoresist 25
2.1.3 Developing 26
2.2 Etching 26
2.2.1 Wafer Etching 26
2.2.2 Photoresist Stripping 27
2.3 Chemicals Used in Photolithography and Etching Process Steps 28
2.4 Routine Equipment Cleaning and Maintenance 29
2.5 Transfer of the Wafer Between Process Steps and Potential Nonroutine Releases/Exposures 30

3 OVERALL APPROACH AND GENERAL FACILITY ESTIMATES 31

3.1 Introduction to the General Facility Estimates 31
3.2 Daily Use Rate of Photoresist (Q_{photo_day}) 32
3.3 Number of Days of Photoresist Application ($TIME_{apply\_days}$) 34
3.4 Daily Use Rate of Chemical of Interest (Q_{chem_day}) 34
3.5 Number of Sites (N_{sites}) 35
3.6 Annual Number of Photoresist Containers Emptied per Facility ($N_{cont\_site\_yr}$) 37

4 ENVIRONMENTAL RELEASE ASSESSMENTS 39

4.1 Control Technologies 40
4.2 Container Residues Released to Water, Incineration, or Landfill (Release 1) 40
4.3 Equipment Cleaning Residues Released to Incineration or Landfill (Release 2) 42
4.4 Excess Photoresist (Spin-off) Released to Incineration (Release 3) 43
4.5 Residual Photoresist Contained in Waste Developer Solution Released to Water (Release 4) 44
4.6 Residual Photoresist Contained in Waste Etching and Stripping Solutions Released to Water (Release 5) 44

5 OCCUPATIONAL EXPOSURE ASSESSMENTS 46

5.1 Personal Protective Equipment 47
5.2 Number of Workers Exposed Per Site 48
5.2.1 Equipment Operators 49
5.2.2 Equipment Maintenance/Waste Management Technicians 50

5.3 Dermal Exposure to Liquid Photoresist During Change-out of Empty Photoresist Containers (Exposure A) 51
5.4 Dermal Exposure to Liquid Photoresist During Cleaning/Handling Empty Photoresist Containers (Exposure B) 52
5.5 Dermal Exposure to Residual Photoresist During Routine Equipment Cleaning/Maintenance (Exposure C) 53
5.6 Dermal Exposure to Liquid Photoresist During Change-out of Excess (Spun-off) Photoresist Collection Containers (Exposure D) 54
5.7 Dermal Exposure to Residual Photoresist During Change-out of Waste Solvent Collection Containers (Exposure E) 55
5.8 Dermal Exposure to Photoresist Coating the Wafer During Nonroutine Transfer of Contaminated Wafers 57

6 SAMPLE CALCULATIONS 58

6.1 General Facility Estimates 58
6.1.1 Daily Use Rate of Photoresist (Q_{photo_day}) 58
6.1.2 Number of Days of Photoresist Application ($TIME_{apply\_days}$) 58
6.1.3 Daily Use Rate of Chemical of Interest (Q_{chem_day}) 58
6.1.4 Number of Sites (N_{sites}) 59
6.1.5 Annual Number of Photoresist Containers Emptied per Site ($N_{cont\_site\_yr}$) 59
6.2 Release Assessments 59
6.2.1 Container Residues Released to Water, Incineration, or Landfill (Release 1) 59
6.2.2 Equipment Cleaning Residues Released to Incineration or Landfill 60
6.2.3 Excess Photoresist (Spin-off) Released to Incineration (Release 3) 60
6.2.4 Residual Photoresist Contained in Waste Developer Solution Released to Water (Release 4) 60
6.2.5 Residual Photoresist Contained in Spent Etching and Stripper Solutions (Release 5) 61
6.3 Occupational Exposure Assessments 61
6.3.1 Number of Equipment Operators per Site 61
6.3.2 Number of Equipment Maintenance/Waste Management Technicians per Site 61
6.3.3 Dermal Exposure to Liquid Photoresist During Change-out of Empty Photoresist Containers (Operators) (Exposure A) 61
6.3.4 Dermal Exposure to Liquid Photoresist During Cleaning/Handling Empty Photoresist Containers (Technicians) (Exposure B) 62
6.3.5 Dermal Exposure to Residual Photoresist During Routine Equipment Cleaning/Maintenance (Technicians) (Exposure C) 62
6.3.6 Dermal Exposure to Liquid Photoresist During Change-out of Excess (Spun-off) Photoresist Collection Containers (Technicians) (Exposure D) 62
6.3.7 Dermal Exposure to Residual Photoresist During Change-out of Waste Solvent Collection Containers (Technicians) (Exposure E) 63

7 DATA GAPS/UNCERTAINTIES AND FUTURE WORK 64

8 REFERENCES 66

APPENDIX A: ESTIMATION EQUATION SUMMARY AND DEFAULT PARAMETER VALUES 69

APPENDIX B: BACKGROUND INFORMATION AND EQUATIONS/DEFAULTS FOR THE STANDARD EPA ENVIRONMENTAL RELEASE AND WORKER EXPOSURE MODELS 75

APPENDIX C: ADDITIONAL REFERENCES 107

APPENDIX D: OTHER SEMICONDUCTOR MANUFACTURING STEPS WITH NO PHOTORESIST RELEASES 110

LIST OF TABLES

Table 1-1. Number of U.S. Facilities and Employees by Employment-Size Class for the Semiconductor and Related Device Manufacturing Industry Sector (NAICS 334413) 19
Table 2-1. Example Chemicals Used in the Photolithography and Etching Process Steps in Semiconductor Manufacturing 29
Table 3-1. Summary of General Facility Parameters 32
Table 3-2. Parameters and Values for Daily and Annual Photoresist Use Rate Calculation 34
Table 4-1. Summary of Photoresist Use Scenario Release Models 40
Table 5-1. Summary of Photoresist Use Scenario Exposure Models 47

LIST OF FIGURES

Figure 2-1. Overall Process Flow Diagram - Semiconductor Manufacturing 21
Figure 2-2a. Photoresist Use in Semiconductor Manufacturing: Photolithography 23
Figure 2-2b. Photoresist Use in Semiconductor Manufacturing: Etching 24

1 INDUSTRY SUMMARY AND BACKGROUND

This section provides an overview of semiconductors and the process by which they are manufactured, as well as information about photoresists and how they are used in the process. This section also briefly describes the U.S. semiconductor manufacturing industry, in terms of the number of facilities and workers.

1.1 Introduction to Semiconductors

Semiconductors can serve one of two purposes: to act as a conductor, by guiding or moving an electrical current, or act as an insulator, by preventing the passage of electricity. Semiconductors are used in computers, consumer electronic products, telecommunication equipment, industrial machinery, transportation equipment, and military hardware. In these products, semiconductors perform functions such as information processing, display purposes, power handling, data storage, signal conditioning, and conversion between light and electrical energy sources [USEPA, 1995].

Semiconductors are created on polycrystalline *wafers*. A single 300-mm silicon wafer can produce several hundred chips. Each chip can contain tens of millions of transistor circuits [Shah, 2006]. These circuits are created using the *photolithography* process, described in this ESD. Silicon has traditionally been the substrate used to manufacture semiconductors; recently, other materials such as gallium arsenide (GaAs) and indium phosphide (InP) have been used as substrates. These wafers are formed by chemically polishing and grinding a crystal ingot (e.g., comprised of polycrystalline silicon) until it has a mirror-like luster.

1.2 Manufacture of Semiconductors

The semiconductor manufacturing process comprises a variety of distinct processing steps resulting in a range of operations that may occur at a single plant or in varying operations at multiple plants. An average semiconductor manufacturing process consists of hundreds of steps, many of which may be repeated several times during the production process.

Through a series of physical and chemical processes, hundreds of thousands of miniature transistors are created on the wafer. Most semiconductor production lines use several basic steps to transform a silicon wafer into a semiconductor. Typically, it takes 10 to 30 days to complete the manufacture of a semiconductor [Intersil, 2001]. The transistor is constructed on the wafer using the following steps [USEPA, 1995]:

- Oxidation – Silicon dioxide is grown or deposited on the wafer to provide a protective coating or insulation.

- Photolithography – A pattern is created on the wafer using photoresist chemicals. Photoresist chemicals are released during the photolithography steps of photoresist application, development, and stripping.

- Doping – Diffusion or ion implantation techniques introduce impurities to the wafer to alter the properties to produce a specific integrated circuit.

- Thin Film Deposition – Thin layers of various metals are deposited to create the semiconductor or to serve as a mask for a particular sector of the wafer [Shah, 2006]. A mask protects one area of the wafer while work is performed on another portion.

- Etching – Specific unwanted areas of silicon substrate or deposited film are removed to expose an underlying material or allow another material to be deposited in the etched material's place.

- Metallization – Conductive metal is deposited onto the wafer to form the conductive layers of the chip. While aluminum has been the metal of choice, modern devices are now using copper as the conductor. A variety of techniques, including evaporation, electrodeposition, electroplating, and chemical vapor deposition, are used to deposit the metal.

- Chemical Mechanical Planarization (CMP) – Excess material is removed from the surface of the wafer so that the product has a flat, uniform surface.

Semiconductor manufacturing is an iterative process in which these steps, with the exception of oxidation, are repeated to build transistors in multiple layers on wafers.

A *clean environment* is essential for manufacturing semiconductors. Flaws in the wafer surface or contamination of the materials used can result in “opens” or “shorts” in the transistor circuits, causing them to be unusable. [Shah, 2006] Therefore, current semiconductor fabrication facilities (i.e., ‘fabs’) are built to Class-1 cleanroom specifications, which means there is no more than one particle larger than 0.5-micron in one cubic foot of air. In addition, cleaning operations precede and follow most of the manufacturing process steps. Wet processing, during which wafers are repeatedly immersed in or sprayed with solutions, is commonly used to minimize the risk of contamination. In addition, many processes operate within a positive pressure environment [SIA, 2005].

During the photolithography step, a light-sensitive photoresist is applied to the wafer via a *spin coating* process. Between 1.5 to 5 mL of liquid photoresist is dispensed onto a wafer spinning at high speed on a vacuum chuck [SIA, 2003], which allows the photoresist to coat the wafer surface uniformly.

After undergoing spin coating, the wafer is “soft baked” to remove most of the solvent in the photoresist. The solid components of the resist remain on the wafer surface and are subsequently exposed to light in a specific pattern. The photoresist undergoes a chemical reaction only in those areas of the wafer surface that is exposed to the light (e.g., a positive photoresist will become more soluble in those exposed areas).

After some time, the exposed wafer is then "hard baked" to improve the resist adhesion and prepare the coated surface for further processing. A developer solution is used to remove a portion of the exposed positive photoresist (or the unexposed negative photoresist) from the wafer in the given pattern. The wafers then go through other process steps (e.g., doping and thin film deposition), including another bake step, prior to the etching and metallization steps [Shah, 2006]. At this point, the remaining photoresist is removed from the wafer in a dry or wet stripping process step following the etching.

Section 2.0 provides additional descriptions of the photolithography and etching processes, including the specific sources of release and potential occupational exposures to the photoresist. As previously stated, the scope of this ESD does not include methods for estimating the releases and exposures to types of chemicals used in semiconductor manufacturing, other than the photoresist. Appendix D contains additional information about other process steps used in the manufacture of semiconductors.

1.3 Overview of Photoresists

A typical photoresist contains between 15 and 40 percent solids[1] suspended in a solvent [Courtney, 1994]. This ESD does not address releases of or inhalation exposures to the volatile solvent portion of the photoresist.

Photoresists are generally classified by how the chemical responds to radiation. Two types of photoresists, positive and negative, are used:

- *Positive* photoresists are chemicals that are made more soluble upon exposure to radiation. The developing process removes the photoresist that was exposed to radiation. These photoresists consist of a photoactive compound, base resins, organic carrier solvents, stabilizers, polymerization inhibitors, viscosity control agents, dyes, and plasticizers [Courtney, 1994] [Eastman, 2002].

- *Negative* photoresists are chemicals that crosslink and become insoluble in developer solutions upon exposure to radiation [Shah, 2006]. The developing process removes the photoresist that was protected from radiation. Polyisoprene is present in many negative photoresists. These photoresists consist of photosensitive compounds, nonphotosensitive compounds, viscosity control agents, dyes, and carrier solvents. Negative photoresists typically use azides for photosensitive compounds [Courtney, 1994].

---

[1] The Semiconductor Industry Association (SIA) indicates that 20 percent solids may be a reasonable average based on anecdotal information [SIA, 2003].

Positive photoresists are the most prevalent used by industry [GA Tech, 2000]. Chemicals currently used as photoresists include polyalkylaldehyde, isoprene, and polymethacrylate.

1.4 Overview of the Semiconductor Manufacturing Industry

Semiconductor manufacturing facilities fall under North American Industry Classification System (NAICS) code 334413 – Semiconductor and Related Device Manufacturing[1]. According to the U.S. Census Bureau's 2004 *County Business Patterns* (CBP), there are 955 semiconductor manufacturing facilities in the United States, employing a total of 141,157 people [USCB, 2004a]. However, according to SIA, because the establishments encompass design centers, sales offices, and warehouses as well as chip manufacturing establishments, and because "it is unlikely that any facility with less than 50 employees could support semiconductor manufacturing," those establishments with under 50 employees should not be considered when determining the total number of chip manufacturing establishments [SIA, 2003]. According to the U.S. Census Bureau, there were 268 U.S. semiconductor manufacturing facilities (28 percent) with 50 or more employees operating in 2004.

Table 1-1 shows the distribution of facilities and employees, based on the employment-size class (i.e., the number of employees at each facility). Note that 50 percent of the total employees in the industry work at the largest three percent of manufacturing facilities.

Table 1-1. Number of U.S. Facilities and Employees by Employment-Size Class for the Semiconductor and Related Device Manufacturing Industry Sector (NAICS 334413)

Employment -Size Class	1-4	5-9	10-19	20-49	50-99	100-249	250-499	500-999	≥1,000	Total
Number of Facilities (% of total)	258 (27%)	125 (13%)	145 (15%)	159 (17%)	88 (9%)	65 (7%)	43 (5%)	43 (5%)	29 (3%)	955 (100%)
Number of Employees (% of total)	435 (0.3%)	848 (0.6%)	2,005 (1%)	4,780 (3%)	6,182 (4%)	10,310 (7%)	15,181 (11%)	30,744 (22%)	70,672 (50%)	141,157 (100%)

Source: USCB, 2004a.

---

[1] The industry sector, defined by NAICS 334413, "…comprises establishments primarily engaged in manufacturing semiconductors and related solid state devices. Examples of products made by these establishments are integrated circuits, memory chips, microprocessors, diodes, transistors, solar cells, and other optoelectronic devices." [USCB, 2004b].

2 PROCESS DESCRIPTION

This ESD describes the sources of release and exposure to the *nonvolatile* components of photoresists formulation used in semiconductor manufacturing. It does not discuss the following: the manufacture of the chemical raw materials used in the photoresist, the formulation of the photoresist product, the volatile (i.e., solvent) components of the photoresist, or information about other types of chemicals used in the semiconductor manufacturing process (e.g., developer solution, etchant, and stripping solution).

The information presented in this section is primarily based on the following sources: the *Emergency Planning and Community Right-to-Know Act (EPCRA) Section 313 Reporting Guidance for Semiconductor Manufacturing* [USEPA, 1999], the Office of Compliance Sector Notebook Project's *Profile of the Electronics and Computer Industry* [USEPA, 1995], and the Semiconductor Industry Association (SIA).

As described in Section 1.2, the manufacture of a semiconductor chip involves several basic process steps (see Figure 2-1):

- Oxidation;
- Photolithography;
- Doping;
- Thin Film Deposition;
- Etching;
- Metallization; and
- Chemical Mechanical Planarization (CMP).

Semiconductor manufacturing is an iterative process, as shown in Figure 2-1. The steps bulleted above are repeated to build transistors in multiple layers on wafers [SIA, 2003]. This ESD describes the use of photoresists in the photolithography step, as well as the potential release and exposure points within the photolithography step and in the subsequent etching step. These two steps are shown in bold in Figure 2-1.

As previously mentioned, the quality and performance of the semiconductor is extremely dependant upon the purity of the wafer surface and the materials used; therefore, these process steps are nearly always performed within an enclosed, Class-1 cleanroom environment. In addition, several of the above steps include cleaning, in which the wafer is rinsed in a solution to remove the various contaminants that may adversely affect the final integrated circuit's electrical performance. Each wafer is cleaned prior to photolithography processing by placing it into inorganic or organic cleaning solutions. The process is typically automated. Rarely (usually in older facilities), workers manually place the wafer into these solutions, and then transfer the wafer to the spin-coat apparatus where the photoresist chemical is added [Shah, 2006].

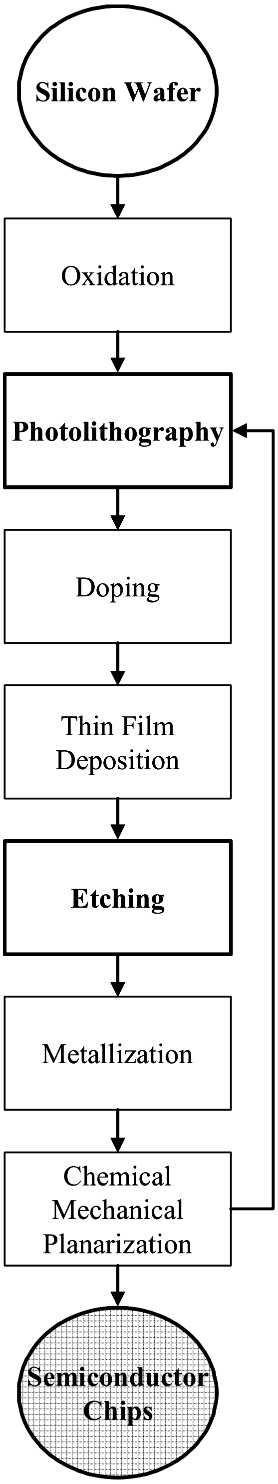


Figure 2-1. Overall Process Flow Diagram - Semiconductor Manufacturing[1]

The two primary semiconductor manufacturing processes that potentially release photoresist are photolithography and etching. The photolithography process steps are as follows:

---

[1] Wafers undergo multiple iterations of the steps from photolithography to CMP, as indicated by the return arrow.

- Photoresist application (i.e., spin-coat) (releases excess photoresist and volatile component vapors);
- Pre-exposure (i.e., soft) bake (releases volatile component vapors);
- Image application (i.e., exposure);
- Post-exposure (i.e., hard) bake (releases remaining volatile component vapors); and
- Developing (releases photoresist contained in developer or alkaline solution) [Shah, 2006].

After the photoresist steps, the wafer undergoes a post-develop bake step and other processing steps before the etching process, which includes the following steps:

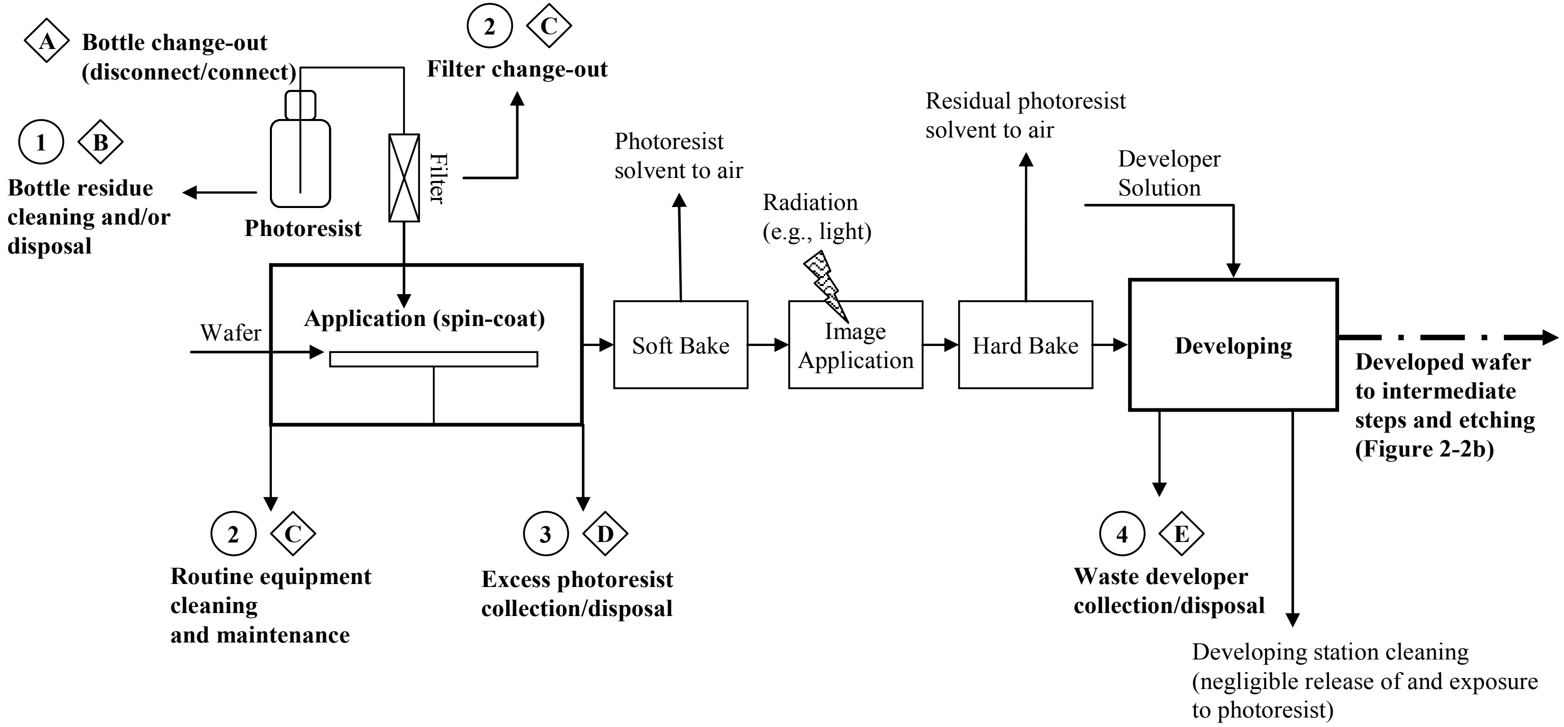
- Etching (releases photoresist contained in waste etchant); and
- Stripping (releases remaining photoresist in waste stripping solution or gas) [Shah, 2006].

After etching, the wafer undergoes other processing before it is finished; however, no other release of photoresist is expected in these final process steps. Flow diagrams, including potential release points, for the photolithography and etching processes are presented in Figures 2-2a and 2-2b, respectively.

The following subsections describe typical operations, chemicals used, and potential release and exposure points during the photolithography and etching steps.

2.1 Photolithography

Photolithography is used in semiconductor manufacturing to form surface patterns on the wafer. These patterns allow various materials to be deposited on or removed from select, precise locations on the wafer. The photolithography process includes several steps: photoresist application, pre-expose (soft) bake, image application (exposure), post-expose (hard) bake, and developing. The number of photolithography steps required depends on the type of semiconductor product (e.g., transistors, integrated circuit) that is being manufactured. The potential releases of photoresist from the photolithography step and potential worker dermal exposures associated with photolithography are illustrated in Figure 2-2a and described below.



○ = Environmental Releases:

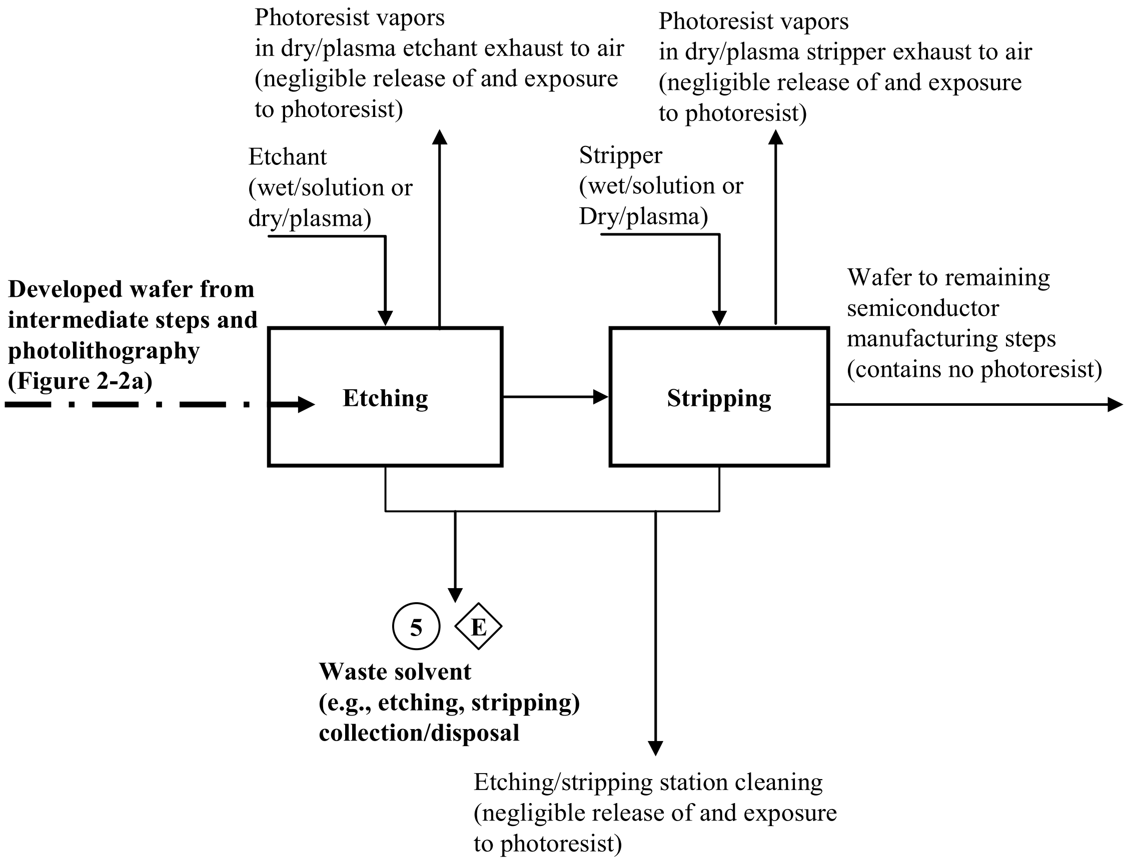
1. Residue in empty photoresist transport container (bottle) released to water, incineration, or landfill.
2. Equipment cleaning and routine maintenance (including supply line filter change-out) resulting in photoresist residues released to incineration or landfill.
3. Excess (spun-off) photoresist released to incineration.
4. Waste developer solvent containing residual photoresist released to water.

(Release 5 is illustrated in Figure 2-2b.)

◇ = Occupational Exposures:

A. Potential dermal exposure to liquid photoresist during container change-out.
B. Potential dermal exposure to liquid photoresist during container cleaning or disposal.
C. Potential dermal exposure to liquid photoresist during routine equipment cleaning/maintenance (including change-out of supply-line filters).
D. Potential dermal exposure to liquid photoresist during excess photoresist collection vessel change-out/routine maintenance.
E. Potential dermal exposure to residual photoresist during waste solvent (e.g., developer, etching, stripping) collection vessel change-out/routine maintenance.

Figure 2-2a. Photoresist Use in Semiconductor Manufacturing: Photolithography



○ = Environmental Releases:

(Releases 1 through 4 are illustrated in Figure 2-2a.)

5. Waste etching/stripping solvents containing residual photoresist released to water or recycle.

◇ = Occupational Exposures:

(Exposures A through E are illustrated in Figure 2-2a.)

E. Potential dermal exposure to residual photoresist during waste solvent (e.g., developer, etching, stripping) collection vessel change-out/routine maintenance.

Figure 2-2b. Photoresist Use in Semiconductor Manufacturing: Etching

2.1.1 Photoresist Application

In this process, the photoresist container is connected to the dispensing apparatus and the liquid photoresist is applied to the wafer on a spin track. Photoresists are usually packaged in one-liter or one-gallon glass or plastic bottles or in NOW Packs ranging from one to five gallons. All of these container types are commonly outfitted with a quick-connect cap that allows the bottle to be directly attached to the equipment (Exposure A) [SIA, 2006] [Shah, 2006].

Because the cost of photoresist is relatively high (e.g., $0.40 to $1.25/mL) [SIA, 2006], nearly all systems are designed to remove as much of the material from the container as possible through a variety of methods and devices. When the container is empty, it is disconnected from the equipment, capped, and bagged (or otherwise packaged) for transfer off site for incineration or washing/recycling [SIA, 2006] [Spinillo, 2005]; facilities might also rinse the bottles on site (Release 1, Exposure B) [Shah, 2005].

A fixed amount (on the order of milliliters) of photoresist is metered through a filter and onto the wafer [Spinillo, 2005] using a dropper or syringe-like delivery system [MacCentral, 1997]. The wafer is spun at high speed on a rotating element to coat the wafer surface uniformly. A vacuum holds the wafer in place while spinning. A small amount (between one and seven percent) of the photoresist applied to the wafer remains on the wafer as the surface coating. Most of the excess photoresist that is "spun off" of the wafer is drained into a waste collection device (Release 3); however, some may also collect on the internal walls and parts of spin-coat apparatus, often termed the *spin bowl* (Release 2). Any residual photoresist contained in the supply-line filter is also disposed of when this filter is changed out (Release 2). Workers may be exposed to the photoresist while performing routine maintenance/cleaning of the dispensing and spin-coat apparatus, including the supply line filter change-out (Exposure C) or while changing out the excess photoresist waste collection device (Exposure D).

2.1.2 Soft Bake, Imaging, and Hard Bake of the Photoresist

To remove the residual carrier solvent, the wafers are "soft baked" prior to exposure. During the soft bake, the wafer is heated until the solvent evaporates. After the soft bake, only traces of the carrier solvent remain, and a uniform coating of nonvolatile photosensitive chemicals remain in a layer that is approximately one micron thick [Shah, 2006].

The predefined areas of the wafer are then exposed to ultraviolet or visible light, lasers, or electron beams in either a *flood* or *step and repeat* exposure process to form a pattern. A template mask, which is a glass plate containing an image of the desired circuit pattern, is used to control which portions of the wafer are exposed to the radiation. Radiation effects depend on whether a positive or negative photoresist is applied to the wafer. As previously described, positive photoresist (the most prevalently used type) reacts by becoming more soluble when exposed to light and will be removed during development and etching, while unexposed photoresist will remain on the wafer surface until it is removed in the final stripping step (see Section 2.2.2).

After the imaging step, remaining solvent (usually only trace amounts) is removed in the "hard bake" step and the photoresist is hardened on the wafer surface.

No release or exposure to the nonvolatile photoresist chemicals is expected during these steps.

2.1.3 Developing

The wafer surface, now containing the hardened exposed and unexposed portions of the photoresist, is either dipped or sprayed with developer solution to dissolve the unwanted portion of the photoresist chemical, yielding a stencil for further processing steps. For example, if a positive photoresist was used, only the areas of the wafer in which the photoresist was exposed to the light/radiation will be removed in this step.

The portion of photoresist that is removed from the wafer during this step is contained with the waste developer in a collection tank. Process waste solvents are often collected via a closed line system and transferred to a wastewater treatment system (Release 4) [McCoy, 2005]. Alternatively, the waste solvents are transferred into appropriate drums or other containers, which are later sent off site for disposal [SIA, 2006]. Workers may be exposed to residual photoresist contained in the developer bath while handling or performing maintenance on the waste solvent containers or collection system (Exposure E).

Workers may also be exposed to residual photoresist when cleaning the developer station; however, the concentrations of photoresist present in the equipment residues are expected to be small. Therefore, the release of and exposure to the photoresist during developer station cleaning activities are negligible [Shah, 2006].

Note: this ESD describes methods for estimating the releases of and exposures to the residual photoresist chemical that is contained in the waste developer solution. It does not cover methods for estimating the amount of waste developer solution released or for estimating workers' exposures to the developer solution.

2.2 Etching

The etching step involves etching the wafer surface, then stripping the surface of remaining photoresist and other materials. The potential release of nonvolatile photoresist chemicals from these two processes and the potential worker dermal exposure to the photoresist are illustrated in Figure 2-2b and described below.

2.2.1 Wafer Etching

Etching chemically removes specific unwanted areas of silicon substrate or deposited film so that an underlying material may be exposed or another material may be deposited in the etched material's place. Etching is usually conducted after a photoresist pattern has been applied, so that the etching is done in specific areas.

Etching may be performed using solutions of acids, bases, or oxidizers (i.e., wet etching) or using various gases (usually halogenated) in a plasma environment (i.e., dry etching). During wet etching, acid solutions selectively remove metal, thus creating a pattern on the wafer. In dry etching, halogenated gases are excited in plasma so that they split apart, forming reactive halogen radicals that etch the surface of the wafer.

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

The waste etching solution will also contain the film removed from the wafer, including a portion of the photoresist. As with the developer solution, these waste solvents are collected via a closed line system and transferred to a wastewater treatment system [McCoy, 2005] or are transferred into appropriate drums or other containers, which are later sent off site for disposal (Release 5) [SIA, 2006]. Workers may be exposed to residual photoresist while handling or performing maintenance on the waste solvent containers or collection system (Exposure E).

Note: this ESD describes methods for estimating the releases of and exposures to the residual photoresist chemical that is contained in the waste etching and stripping solutions. It does not cover methods for estimating the amount of waste etchant released or for estimating workers' exposures to the etchant chemicals.

2.2.2 Photoresist Stripping

Some residual photoresist may remain on the wafer after etching and is removed in a procedure called *stripping*. Two types of stripping may be used in the process, wet or dry. Wet stripping uses a wide variety of chemical resist strippers (e.g., solvents, acids, bases) to dissolve the photoresist. Dry stripping uses plasma gas, which reacts with the photoresist, yielding gases that may be removed with a pump. Selecting the appropriate stripping material is important to ensure the base material of the wafer is not removed.

In the case of dry/plasma stripping, photoresist vapors are typically captured by the exhaust, which is scrubbed and incinerated (or released to air); however, the amount of photoresist released is considered negligible [Shah, 2006].

The waste stripping bath contains essentially all of the photoresist that remained on the wafer and is collected via a closed line system and transferred to a wastewater treatment system [McCoy, 2005] or is transferred into appropriate drums or other containers, which are later sent off site for disposal (Release 5) [SIA, 2006]. Workers may be exposed to the residual photoresist while handling or performing maintenance on the waste solvent containers or collection system (Exposure E).

Workers may also be exposed to residual photoresist when cleaning the etching/stripping station; however, the concentrations of photoresist present in the equipment residues are expected to be small. Therefore, the release of and exposure to the photoresist during the cleaning of the etching/stripping station are negligible [Shah, 2006].

Note: this ESD describes methods for estimating the releases of and exposures to the residual photoresist chemical that is contained in the waste etching and stripping solutions. It does not cover methods for estimating the amount of waste stripper released or for estimating workers' exposures to the stripper chemicals.

2.3 Chemicals Used in Photolithography and Etching Process Steps

Photoresist chemicals are polymer-based liquids in which photoactive molecules are dissolved in a carrier solvent. Photoresists generally comprise base resins, plasticizers, photosensitive compounds, and other additives (e.g., stabilizers, viscosity control agents, dyes) contained in a carrier solvent [Courtney, 1994].

The solvent fraction of the photoresist serves only as a carrier for the photosensitive compounds within the resist. Solvents aid in evenly distributing the resist over the wafer during spin coating operations. A typical photoresist contains between 15 and 40 percent solids[1] suspended in a solvent-based chemical [Courtney, 1994].

Table 2-1 lists examples of chemicals that are used in the photolithography and etching process steps. Currently, EPA has limited information on the specific chemicals typically found in photoresist formulations. The photoresist chemicals listed in Table 2-1 are all polymers that possess a wide range of molecular weights, vapor pressures, and other physical properties. These nonsolvent photoresist chemicals are expected to be of high, variable molecular weight and have negligible vapor pressures.

As previously stated, this ESD describes methods for estimating the releases of and exposures to the nonvolatile photoresist chemicals used in semiconductor manufacturing. It does not cover methods for estimating the amounts of other process chemicals that are released or for estimating workers' exposures to these other process chemicals.

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[1] The SIA indicates that 20 percent solids may be a reasonable average based on anecdotal information [SIA, 2003].

Table 2-1. Example Chemicals Used in the Photolithography and Etching Process Steps in Semiconductor Manufacturing

Photoresists	Developer	Solvents and Cleaning Agents
Positive: Ortho-diazoketone Polymethacrylate Polyfluoroalkylmethacrylate Polyalkylaldehyde Polycyanoethylacrylate Polymethylmethacrylate Poly (hexafluorobutylmethacrylate) Novalac resin **Negative:** Isoprene Ethyl acrylate Glycidylmethacrylate Copolymer-ethylacrylate	**Positive:** Sodium hydroxide Potassium hydroxide Silicates Ethylene glycol Ethanolamine Isopropyl alcohol Phosphates Tetramethyl-ammonium hydroxide Alkyl amine Ethyl acetate Methyl isobutyl ketone **Negative:** Xylene Aliphatic hydrocarbons N-Butyl acetate Isopropyl alcohol Stoddard solvent	Deionized water Detergent Isopropyl alcohol Acetone Ethanol Hydrofluoric acid Sulfuric acid Hydrogen peroxide Hydrochloric acid Nitric acid Ammonium hydroxide Hexamethyldisilazane Xylene n-Butyl acetate Propylene glycol ether Ether acetate Ethyl lactate 2-heptanone Gamma butyrolactone
Etching		**Stripping**
Wet: Sulfuric acid Phosphoric acid Hydrogen peroxide Nitric acid Hydrofluoric acid Hydrochloric acid Ethylene glycol Hydroxide solutions Solutions of ammonium, ferric, or potassium compounds	**Dry:** Chlorine Hydrogen bromide Carbon tetrafluoride Sulfur hexafluoride Trifluoromethane Fluorine Fluorocarbons Boron trichloride Argon Hydrogen Oxygen Helium	**Wet:** Acids Alkalines Potassium hydroxide Monoethanolamine Acetone Sulfuric acid **Dry:** Oxygen

Source: Rhodia, 2003.

2.4 Routine Equipment Cleaning and Maintenance

Due to its complexity, as well as the need to keep the semiconductor manufacturing environment clean, the photolithography and other process equipment is cleaned and maintained on a regular basis. The most significant source of photoresist release and exposure during equipment cleaning occurs in maintaining the application/spin coating apparatus, which includes the periodic change-out of the supply line filter (Release 2, Exposure C).

The equipment and parts are cleaned monthly or more frequently if the photoresist has a higher viscosity (e.g., biweekly or weekly). The supply line filter is changed annually, and is often contained in a cartridge with quick-connect components that prevent spilling and allow the filter to be handled without exposing the worker to the wet filter [Spinillo, 2005].

2.5 Transfer of the Wafer Between Process Steps and Potential Nonroutine Releases/Exposures

As shown in Figure 2-1, other manufacturing steps occur between the photolithography and etching steps. In most cases, the entire process is contained within a sealed line and the wafer manipulated robotically between process steps. No releases of or exposures to the nonvolatile photoresist chemicals are expected to occur during these process steps.

Again, because the quality of the final product depends on the purity of the wafer surface and all materials used in the manufacturing process, human involvement in the process is minimized as much as possible. Actual contact with the photoresist on the wafer surface is unlikely and would damage it beyond its usefulness, requiring reprocessing. When wafers are reprocessed, all photoresist is stripped from the surface using solvents, inorganic materials, and/or plasma gas. The waste from reprocessing is either collected for treatment on site or for shipment off site, as described in Section 2.2.2 [SIA, 2006].

For this reason, wafers are never manually transferred between process steps except perhaps in instances of nonroutine system failure and repair. When the wafers are removed from the equipment enclosures, they are typically enclosed in a “microenclosure” (often termed a *wafer boat*) that may hold up to 25 wafers and is designed to transport the wafers without interacting with the environment in the facility [SIA, 2006].

In older facilities, small cassettes of wafers may be manually carried between process steps. While these older cassettes are open, they are within a cleanroom and the workers handling the cassette are required to wear gloves and other personal protective equipment (PPE) that would prevent contamination of the wafer surface as well as exposure to the photoresist [SIA, 2006].

EPA has received no additional information to date regarding what portion of a facilities’ wafers are expected to require reprocessing due to contamination or equipment failure. For the purposes of this ESD, it is assumed that the nonroutine releases and/or exposures are rare to the point of being negligible.

3 OVERALL APPROACH AND GENERAL FACILITY ESTIMATES

This ESD presents a standard approach for estimating environmental releases of and worker exposures to photoresist chemicals used in the manufacture of semiconductors. The ESD covers the use of the photoresist in the photolithography process and its release from the subsequent etching process.

The estimation methods described in this document utilize available industry-specific information and data to the greatest extent possible; however, EPA acknowledges several areas in which additional photoresist formulation and semiconductor manufacturing industry data would improve the assessment methodology presented in this ESD. These data needs are summarized in Section 7 of this ESD. EPA intended the default values cited throughout this ESD to be used only when appropriate site-specific or industry-specific information is not available.

Because this ESD presents several alternative default assumptions or values for some estimation parameters, selecting different defaults will affect the final assessment results differently. For example, conservative or high-end daily use rates will result in conservative release estimates. Alternatively, average or median use rates will result in release estimates that are more “typical” of the industry. This ESD presents available data that support alternative input values.

This section presents general facility calculations, which estimate the daily use rate of the photoresist containing the chemical of interest, the number of semiconductor manufacturing sites that use the photoresist, and the number of days the photoresist is expected to be used in the semiconductor manufacturing process.

Section 4 of the ESD presents the environmental release assessment, which uses the general facility estimates to estimate the quantity of photoresist chemical released from various points in the semiconductor manufacturing process and the most likely media of release for each release source.

Section 5 of the ESD presents the occupational exposure assessment, which uses both the general facility estimates and release estimates to estimate the number of workers potentially exposed while performing various process activities and the corresponding potential level (quantity) of dermal exposure. Note that inhalation exposure to nonvolatile photoresist chemicals is not expected.

3.1 Introduction to the General Facility Estimates

Through the remainder of this section, EPA utilized available photoresist and semiconductor industry data on photoresist uses rates to estimate the number of semiconductor manufacturing sites that may use a particular photoresist containing the chemical of interest. The default assumptions and calculations described in this section are also used to estimate the use rate for the chemical of interest and the number of shipping containers that are transferred into the operation annually.

The general facility estimates presented in this section are based on the following key assumptions from recent information gathered in the United States. [SIA, 2003]:

- A facility applies photoresists to wafers at a rate of 100 to 1,000 times per hour, depending on the size of the plant;
- A facility applies photoresists to wafers for 20 to 24 hours per day;
- A facility dispenses photoresists to wafers at a rate of 0.5 to 5 mL per application; and
- A facility applies photoresists to wafers for 250 to 360 days per year.

Table 3-1 summarizes the general facility estimates and the ESD section in which they are discussed. In addition, Table A-4 in Appendix A summarizes the default values used as inputs for each of the general facility estimates, accompanied by their references.

Table 3-1. Summary of General Facility Parameters

Parameter	Description	ESD Section
Q_{photo_day}	Average daily dispense (or use) rate of the photoresist containing the chemical of interest per facility (kg photoresist applied/site-day)	3.2
$TIME_{apply\_days}$	Number of days of photoresist application per year (days/year)	3.3
Q_{chem_day}	Daily dispense (or use) rate of the chemical of interest within the photoresist (kg chemical/site-day)	3.4
N_{sites}	Number of facilities applying the chemical of interest within photoresists to manufacture semiconductors (sites)	3.5
$N_{cont\_site\_yr}$	Annual number of chemical-containing photoresist containers emptied per facility (container/site-yr)	3.6

The method described in the remaining subsections incorporates certain assumptions in cases where industry-specific data were not found. These key assumptions are presented throughout this section as well as a discussion of their uncertainties and potential effects on the estimates.

3.2 Daily Use Rate of Photoresist (Q_{photo_day})

The amount of photoresist dispensed (or *used*) per day at a semiconductor manufacturing facility depends primarily upon the number of photoresist applications to wafers per hour, the amount of photoresist dispensed per application, and the number of application hours per day. Equation 3-1 expresses this estimation method, and Table 3-2 shows a range of parameter values and associated estimated application rates.

$$Q_{photo\_day} = N_{apply} \times TIME_{apply\_hour\,s} \times \left(\frac{Q_{apply}}{1{,}000\,\text{mL/L}} \right) \times RHO_{photo} \qquad (3\text{-}1)$$

Where:

- Q_{photo_day}= Average daily dispense/use rate of the photoresist per facility (default: 36 kg photoresist dispensed/site-day (refer to Table 3-2))
- N_{apply} =Number of applications per site, per hour (default: 1,000 applications/site-hr) [SIA, 2003]
- $TIME_{apply\_hours}$ = Hours of application per day (default: 24 hrs/day) [SIA, 2006/2003]
- Q_{apply} =Quantity of photoresist dispensed per wafer application (default: 1.5 mL photoresist dispensed/application) [SIA, 2003]
- RHO_{photo} = Photoresist density (default: 1 kg photoresist/L)

The density of water (1 kg/L) may be used as a default value when specific information on the photoresist is not available, as many photoresist chemicals have densities similar to that of water. Examples of photoresist densities include: polymethacrylate (1.19 kg/L), glycidylmethacrylate (1.04 kg/L), and ethyl acrylate (0.92 kg/L).

Note: This daily dispense or use rate is not equivalent to the amount of photoresist that is purchased and received at each site. As explained later in this section, a residual amount of photoresist is expected to remain in the container and not dispensed into the process. On an annual basis, the difference between the amount received at the facilities the amount *used* is the residual amount of photoresist that remains in the containers.

Although each parameter in Equation 3-1 has a range of values, it is not appropriate to use the ranges' high values simultaneously to estimate a conservative average daily use rate. For example, the large-scale facilities with higher numbers of applications per hour are expected to use lower quantities of photoresist per application. Table 3-2 shows example facility scales.

Table 3-2. Parameters and Values for Daily and Annual Photoresist Use Rate Calculation

Manufacturing Scale	N_{apply} (applications/ site-hr)[a]	$TIME_{apply\_hours}$ (hours/day)	Q_{apply} (ml/application)	Q_{photo_day} (kg/site-day)	$TIME_{apply\_days}$ (days/yr)
Niche[b]	100	20	5	10	250
Large Scale[c] – low end	500	22	3	33	300
Large Scale[c] – high end	***1,000 (default)***	***24 (default)***	***1.5 (default)***	***36 (default)***	***360 (default)***

Source: SIA, 2003.

a - Applications per site-hr (N_{apply}) is the product of wafer starts per site-hr and applications per wafer start.

b - Niche production is limited in scale. The product could be older but still in demand, or it could be newer but produced in limited quantities such as ASICs (application-specific integrated circuits).

c - The two large-scale parameter sets are meant to capture the *range* of current manufacturing facilities producing devices on a number of different wafer sizes. The differences between the two ends of the "large" spectrum relate to the number of photolithography application steps, the amount of photoresist dispensed or used per application (Q_{apply}), and the range of operating characteristics (hrs/day, days/year). Applications per site-hr (N_{apply}), hours of operation per day ($TIME_{apply\_hours}$), and days of operation per year ($TIME_{apply\_days}$) are typically higher for newer large facilities. Photoresist dispensed or used per application (Q_{apply}) is typically lower for newer large facilities.

3.3 Number of Days of Photoresist Application ($TIME_{apply\_days}$)

If specific information is not available to estimate the number of days of photoresist application per year ($TIME_{apply\_days}$), a default should be selected from Table 3-2:

- $TIME_{apply\_days}$ = Days of photoresist application per year (default: 360 days/yr; refer to Table 3-2)

Note that $TIME_{apply\_days}$ must be associated appropriately with the daily photoresist use rate (Q_{photo_day}) estimated in Section 3.2 to reflect the total annual use rate.

3.4 Daily Use Rate of Chemical of Interest (Q_{chem_day})

To estimate the amount of chemical of interest contained in the photoresist formulation that is dispensed (or *used*) in the process, the daily use rate of the photoresist (Q_{photo_day}) is multiplied by the chemical's concentration (mass fraction) in the photoresist (F_{chem}).

Also, facilities may use multiple photoresist products; therefore, the chemical of interest may not be in all of these photoresists. If appropriate, a correction factor could be applied to adjust Q_{photo_day} to that of photoresist containing the chemical of interest (e.g., (estimated number of photoresist applications containing the chemical of interest per site, per year)/(total number of photoresist applications per site, per year) or ($N_{app\_chem}/N_{app\_photo}$)).

No information has been found that allows EPA to estimate the number of photoresist applications that are made to each wafer, the number of different products manufactured at each site requiring different photoresist formulations, or the fraction of applications that would utilize a particular photoresist formulation (and chemical) as one of multiple available photoresists that could be used at a given facility. If chemical-specific information is not available or not known, a correction factor $N_{app\_chem}/N_{app\_photo}$ of 1 may be assumed.

$$Q_{chem\_day} = Q_{photo\_day} \times F_{chem} \times \frac{N_{app\_chem}}{N_{app\_photo}} \qquad (3\text{-}2)$$

Where:

- Q_{chem_day} = Daily use rate of chemical of interest chemical (kg chemical dispensed/site-day)
- Q_{photo_day} = Daily use rate of photoresist at each facility (kg photoresist dispensed/site-day) (see Section 3.2)
- F_{chem} =Mass fraction of chemical of interest in the photoresist (default: 0.4 kg chemical/kg photoresist (high end) [Courtney, 1994]; alternative fraction: 0.2 kg chemical/kg photoresist [SIA, 2003] [UBA Germany, 2003])
- N_{app_chem} = Number of applications per site, per year of photoresist containing the chemical of interest (default: N_{app_photo} applications/site-yr)
- N_{app_photo} = Number of applications per site, per year of all photoresists (applications/site-yr)

3.5 Number of Sites (N_{sites})

The number of semiconductor manufacturing facilities using the chemical of interest within a photoresist (N_{sites}) depends on the total annual production of the chemical of interest (Q_{chem_yr}) (minus the amount lost (i.e., not used in the process) as residual in empty containers ($F_{container\_disp}$)), the daily use rate of the chemical of interest (Q_{chem_day}), and the annual operating days ($TIME_{apply\_days}$).

Equation 3-3 demonstrates how the number of semiconductor manufacturing facilities estimated to use the photoresist containing the chemical of interest is determined.

$$N_{sites} = \frac{\left(1 - F_{container\_disp}\right) \times Q_{chem\_yr}}{Q_{chem\_day} \times TIME_{apply\_days}} \qquad (3\text{-}3)$$

Where:

- N_{sites}[1] =Number of semiconductor manufacturers using the photoresist that contains the chemical of interest
- $F_{container\_disp}$ = Mass fraction of photoresist lost as residue in empty containers (kg photoresist remaining in container/kg photoresist shipped in container) (See Section 4.2)
- Q_{chem_yr} = Annual production volume of the chemical of interest (kg chemical packaged & sold/yr)
- Q_{chem_day}= Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4)
- $TIME_{apply\_days}$ = Days of photoresist application per year (days/yr) (see Section 3.3)

Note that the calculated value of N_{sites} should not exceed the total number of semiconductor manufacturing facilities known to operate in the United States. See Section 1.4 for additional information on the total number of U.S. semiconductor manufacturers.

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[1] The value for N_{sites} calculated using Equation 3-3 should be rounded up to the nearest integer value. Q_{chem_day} should then be adjusted for the N_{sites} integer value (to avoid errors due to rounding):

$$Q_{chem\_day} = \frac{\left(1 - F_{container\_disp}\right) \times Q_{chem\_yr}}{N_{sites} \times TIME_{apply\_days}}$$

Note: if the number of manufacturing sites and/or application days is known, the previous equation may also be used to estimate Q_{chem_day} for use in subsequent calculations.

Summary of the Relationship of General Facility Parameters

The values for days of application ($TIME_{apply\_days}$), daily use rate of the chemical of interest (Q_{chem_day}), and number of manufacturing sites (N_{sites}) are related. This ESD presents one method for estimating Q_{chem_day} using estimated default values for: 1) the daily amount of photoresist used per site; 2) the total number of days per year the photoresist is applied; 3) the mass fraction of the chemical of interest in the photoresist (F_{chem}); and 4) the mass fraction of photoresist that is NOT used, but is disposed of as residue in the empty containers ($F_{container\_disp}$).

If N_{sites} and $TIME_{apply\_days}$ are known, Q_{chem_day} can be calculated directly without using Equation 3-2. This alternative calculation is:

$$Q_{chem\_day} = \frac{(1 - F_{container\_disp}) \times Q_{chem\_yr}}{N_{sites} \times TIME_{apply\_days}}$$

If N_{sites} is known and $TIME_{apply\_days}$ is unknown, EPA recommends that using the default assumption that the photoresist is applied 360 days per year and Q_{chem_day} be calculated using the above equation.

EPA recommends calculating the chemical of interest throughput based on the methodology presented in Section 3.4, and compare it to the throughput based on number of sites and operating days, as calculated above.

3.6 Annual Number of Photoresist Containers Emptied per Facility ($N_{cont\_site\_yr}$)

The number of photoresist containers emptied annually per site can be estimated based on the chemical of interest's production volume, container size, and concentration in the photoresist. EPA suggests using a default container size of a 1-gallon bottle in the absence of site-specific information [SIA, 2006]. Engineering judgment should be used to determine if another container type or size is more appropriate (e.g., larger jugs or NOW Pack bottles). If the density of the photoresist is not known, the density for water may be used as a default (1 kg/L), consistent with the calculation in Section 3.2.

$$N_{cont\_site\_yr} = \frac{Q_{chem\_yr}}{F_{chem} \times Q_{cont} \times N_{sites}} \quad (3\text{-}4)$$

Where:

- $N_{cont\_site\_yr}$ = Annual number of containers emptied containing chemical of interest per site (containers/site-yr)
- Q_{chem_yr} = Annual production volume of the chemical of interest (kg chemical packaged & sold/yr)
- F_{chem} =Mass fraction of the chemical of interest in the photoresist (kg chemical/kg photoresist) (see Section 3.4)
- Q_{cont}[1] =Mass of the photoresist in the container (kg photoresist/container)
- N_{sites} =Number of semiconductor manufacturers using the photoresist that contains the chemical of interest (see Section 3.5)

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[1] If the mass of the photoresist in each container is not known, it can be calculated using the volume of the container and the density of the photoresist:

$$Q_{cont} = V_{cont} \times RHO_{photo}$$

Where:

- V_{cont} =Volume of photoresist per container (default: 3.8 L photoresist/container (1-gallon bottle) [SIA, 2006]; see Table B-3 in Appendix B for alternative default container volumes.
- RHO_{photo}=Density of the photoresist (see Section 3.2)

4 ENVIRONMENTAL RELEASE ASSESSMENTS

This section presents approaches for calculating the amount of photoresist chemicals released form each release source as well as the most likely receiving media (i.e., air, water, landfill, incineration). The release sources are discussed in the order that they occur in the process (please refer to flow diagrams in Figures 2-2a and 2-2b). The primary sources of releases include container residue, process equipment cleaning/supply-line filter residues, photoresist that does not adhere to the wafer in the application process, spent developer, and spent etching and stripping solutions. Table A-4 in Appendix A lists key default values used for the release estimates, accompanied by their respective references.

All release equations in this section estimate daily rates for a given site. To estimate annual releases for all sites for a given source, the release rates must be multiplied by the number of days of release and by the number of sites using photoresists containing the chemical of interest (N_{sites}) (see Equation 3-3).

For most release sources, this ESD assumes that the number of days of release is the same as the number of days of application. Some of these releases are expected to go to the same medium of release on the same days; therefore, daily and annual releases to a given medium may be summed to yield total amounts released per site, per day and per year, respectively.

Two of the environmental release estimates presented in this document are based on standard EPA release models. The remaining three estimates are based on information obtained from U.S. industry sources. Table 4-1 summarizes the release estimation methods used in this ESD. Section 8 presents a description of the sources reviewed and full citations for those specifically used in these calculations.

Releases to air of nonvolatile photoresist chemicals are generally not expected. While some misting may occur during the spin-coat application of the photoresist, this process is conducted within an enclosed apparatus; therefore, releases of the mist to air are not expected during routine operations. In addition, small amounts of the photoresist may volatilize and be removed during dry/plasma etching and stripping of the wafer surfaces; however, the amount of photoresist in these exhausts are expected to be negligible and no releases to air are expected [Shah, 2006].

Note that the standard model default values cited are current as of the date of this ESD; however, EPA may update these models as additional data become available. EPA recommends using the most current version of the models in these calculations.

EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Appendix B provides additional information on ChemSTEER, including instructions for obtaining the program, as well as background information, model equations, and default values for all standard EPA models.

Table 4-1. Summary of Photoresist Use Scenario Release Models

Release Source #	Description	Model Name or Description[a]	Standard EPA Model (✓)
1	Container residue released to water, incineration, or landfill	EPA/OPPT Small Container Residual Model	✓
2	Equipment cleaning and supply-line filter residues released to incineration or landfill	EPA/OPPT Single Process Vessel Residual Model	✓
3	Excess photoresist (spin-off) released to incineration	Loss rate is based on available industry-specific data	
4	Residual photoresist contained in waste developer solution	Loss rate is based on available industry-specific data	
5	Residual photoresist contained in waste etching and stripping solutions	Loss rate is based on available industry-specific data	

OPPT – EPA's Office of Pollution Prevention and Toxics.
a – Appendix B contains additional detailed descriptions for each of the models presented in this section.

4.1 Control Technologies

EPA collected limited information on the pollution control technologies that are generally expected to be used by semiconductor manufacturers. As described in Section 2, the semiconductor manufacturing process is typically conducted within a closed, positive pressure environment to protect the wafer surface and materials used from contamination. Many of the mechanisms used to protect the process from the external environment also prevent fugitive releases of the chemicals used. General and/or local ventilation systems are also expected to be used at various points along the manufacturing line, particularly in areas where solvent vapors may be expected to be present (e.g., photoresist container connections, wafer bake). Some facilities may operate a wastewater pretreatment system on site, in which aqueous process wastes (e.g., developer, etching and stripping solutions) are treated prior to transfer to a POTW or discharge to surface water.

4.2 Container Residues Released to Water, Incineration, or Landfill (Release 1)

Photoresist is typically supplied to the user in small containers, including one-liter or one-gallon (3.8-liter) bottles and one- to five-gallon (3.8 to 19-liter) NOW Pack bottles with a collapsible internal bladder [CEB, 1994a] [CEB, 2001b] [SIA, 2003]. Potential releases occur from cleanout and/or disposal of the used container. The media of release for this source is uncertain; in these cases, EPA assumes that disposal may be to water, land, or incineration[1].

The amount of liquid photoresist remaining in the containers depends on the size of the container. Based on industry input from SIA, EPA suggests using a default

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[1] Note: available information on industry practices in Germany indicate empty containers are incinerated [UBA Germany, 2003].

container size of 1-gallon bottles in the absence of site-specific information; therefore, the *EPA/OPPT Small Container Residual Model* may be used to estimate this release. The model assumes that up to 0.6 percent of the liquid originally contained in small containers remains as residual after unloading [CEB, 1992]. The rationale, defaults, and limitations of this and alternative container residual models are further explained in Appendix B.

The annual number of containers emptied ($N_{cont\_site\_yr}$) is estimated based on the average annual amount of photoresist received at each semiconductor manufacturing site and the container size (see Section 3.6). EPA recommends assuming 1-gallon (3.8-L) bottles and a density of 1 kg/L (density of water) as defaults, if chemical-specific information is unavailable. If the fraction of the chemical in the photoresist is unknown, assume 40 percent concentration, consistent with Section 3.4 calculations.

If the $N_{cont\_site\_yr}$ value is fewer than the days of application ($TIME_{apply\_days}$), the days of release equal $N_{cont\_site\_yr}$ (as calculated in Equation 3-4) and the daily release is calculated based on the following equation:

$$Elocal_{container\_residue\_disp} = Q_{cont} \times F_{chem} \times F_{container\_disp} \times N_{cont\_site\_day} \quad (4\text{-}1a)$$

This release will occur over [$N_{cont\_site\_yr}$] days/year from [N_{sites}] sites.
Where:

- $Elocal_{container\_residue\_disp}$ = Daily release of chemical of interest from container residue (kg chemical released/site-day)
- Q_{cont} =Mass of the photoresist in the container (kg photoresist/container) (default: use the same value used to estimate $N_{cont\_site\_yr}$ in Section 3.6)
- F_{chem} =Mass fraction of the chemical of interest in the photoresist (kg chemical/kg photoresist) (see Section 3.4)
- $F_{container\_disp}$ = Mass fraction of photoresist remaining in the container as residue (default: 0.006 kg photoresist remaining/kg shipped for bottles [CEB, 1992]; see Appendix B for defaults used for other container types)
- $N_{cont\_site\_day}$ = Number of containers emptied per site, per day (default: 1 container/site-day)

If $N_{cont\_site\_yr}$ is greater than $TIME_{apply\_days}$, more than one container is unloaded per day (i.e., $N_{cont\_site\_day} > 1$). The days of release should equal the days of application, and the average daily release can be estimated based on the following equation:

$$Elocal_{container\_residue\_disp} = Q_{chem\_received\_day} \times F_{container\_disp} \quad (4\text{-}1b)$$

This release will occur over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites.
Where:

- $Elocal_{container\_residue\_disp}$ = Daily release of chemical of interest from container residue (kg chemical released/site-day)
- $Q_{chem\_received\_day}$[1]= Daily amount of the chemical of interest received at the facility, prior to use/application (kg chemical received/site-day)

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[1] The daily amount of chemical received at the facility may be estimated as:

- $F_{container\_disp}$ = Mass fraction of photoresist remaining in the container as residue (default: 0.006 kg chemical remaining in container and released/kg received in full container, for bottles [CEB, 1992]; see Appendix B for defaults used for other container types)

4.3 Equipment Cleaning Residues Released to Incineration or Landfill (Release 2)

The amount of residual photoresist chemical remaining in the application equipment (e.g., spin-coat apparatus, supply line filter) may be estimated using the *EPA/OPPT Single Process Vessel Residual Model.* The model assumes that no more than one percent of the dispensed photoresist (i.e., the daily use rate of the chemical of interest, less the container residue) remains as residue that is released as equipment cleaning waste. Most facilities use various solvents to clean process equipment [ISESH, 2002]. These residues may be released to incineration or landfill[1] [SIA, 2003]. One industry contact estimated that routine cleaning and maintenance activities may take place monthly or more frequently if the photoresist formulation is relatively thick/viscous (e.g., on a biweekly or weekly basis) and that supply line filters are changed out annually [Spinillo, 2005].

As a conservative estimate, daily equipment cleaning may be assumed (i.e., the days of release equal the days of application ($TIME_{apply\_days}$)), and the daily release of chemical residue in the process equipment is calculated using the following equation:

$$Elocal_{equip\_disp} = Q_{chem\_day} \times F_{equip\_disp} \quad (4\text{-}2)$$

This release will occur over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites.

Where:

- $Elocal_{equip\_disp}$ = Daily release of chemical of interest from equipment cleaning (kg chemical released/site-day)
- Q_{chem_day} = Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4)
- F_{equip_disp} = Mass fraction of chemical released as residual in process equipment (default = 0.01 kg chemical released/kg chemical dispensed into the equipment) [CEB, 1992].

$$Q_{chem\_received\_day} = \frac{Q_{chem\_day}}{1 - F_{container\_disp}}$$

Where:

- Q_{chem_day} = Daily use rate of the chemical of interest (kg chemical dispensed/site-day) (see Section 3.4)
- $F_{container\_disp}$ = Mass fraction of photoresist remaining in the container as residue (kg chemical remaining/kg received in full container) (see Section 4.2)

[1] Note: available information on industry practices in Germany indicate these wastes are recycled or incinerated [UBA Germany, 2003].

Note: if it is known that the equipment is cleaned less frequently than each application day, the appropriate number of days of cleaning/release (e.g., 12 days/year (monthly), 26 days/year (biweekly), or 52 days/year (weekly)) should be used in lieu of $TIME_{apply\_days}$ in Equation 4-2 above. In addition, the residues accumulate in the equipment each day that it is not cleaned. If this accumulated amount is not otherwise known, it may be estimated by multiplying the daily amount of residue (as calculated by Equation 4-2) by the number of days of the cleaning interval (e.g., 30 days (monthly), 14 days (biweekly), 7 days (weekly)).

4.4 Excess Photoresist (Spin-off) Released to Incineration (Release 3)

The photoresist is applied by a dispensing apparatus while the wafer is spinning at high speed in an exhausted enclosure. The excess photoresist from the application process is collected from the enclosure and disposed of, typically by incineration[1] [SIA, 2003]. An estimated <u>one to seven percent</u> of the dispensed photoresist containing the chemical of interest may remain on the wafer [SIA, 2003] [ISESH, 2002], and the remaining "spun-off" material is disposed of. As a conservative estimate for water releases, EPA recommends assuming that up to seven percent of the dispensed photoresist remains on the wafer (wastes from developing, etching, and stripping are more likely released to water). Alternatively, incineration releases may be maximized by assuming one percent of the dispensed photoresist remains on the wafer.

Some of this excess photoresist remains in the equipment and is disposed of as cleaning residue (Release 2). Note that the amount of residue disposed of with equipment cleaning wastes is excluded from the amount of collected excess photoresist that is estimated by the following equation:

$$Elocal_{excess\_disp} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times (1 - F_{photo\_wafer}) \qquad (4\text{-}3)$$

This release will occur over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites.
Where:

- $Elocal_{excess\_disp}$ = Daily release of chemical of interest from application excess (kg chemical released/site-day)
- Q_{chem_day} = Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4)
- F_{equip_disp} = Mass fraction of chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into the equipment) (see Section 4.3)
- F_{photo_wafer} = Mass fraction of the photoresist chemical applied that adheres to the wafer surface (default = 0.07 kg chemical adhered/kg chemical applied onto the spinning wafer) [SIA, 2003] [ISESH, 2002]

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[1] Note: available information on industry practices in Germany indicate these wastes are recycled or incinerated [UBA Germany, 2003].

4.5 Residual Photoresist Contained in Waste Developer Solution Released to Water (Release 4)

Developer solutions are a potential source of release of the chemical of interest [ISESH, 2002]. The developer solution is designed to remove either the exposed (positive) or unexposed (negative) photoresist from the wafer. The waste developer solution containing the removed photoresist is expected to be released to water [SIA, 2003]. EPA estimates that 50 percent of the photoresist that adhered to the wafer surface, which was subsequently baked and exposed to light or other energy source, is removed in the development process[1] [CSM, 2002].

The daily release rate of the photoresist chemical of interest (kg/site-day) contained in the waste developer solution can be calculated using the following equation:

$$\text{Elocal}_{\text{developer}} = Q_{\text{chem\_day}} \times \left(1 - F_{\text{equip\_disp}}\right) \times F_{\text{photo\_wafer}} \times F_{\text{photo\_develop}} \qquad (4\text{-}4)$$

This release will occur over [$\text{TIME}_{\text{apply\_days}}$] days/year from [$N_{\text{sites}}$] sites.

Where:

- $\text{Elocal}_{\text{developer}}$ = Daily release of chemical of interest from developing (kg chemical released/site-day)
- $Q_{\text{chem\_day}}$= Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4)
- $F_{\text{equip\_disp}}$= Mass fraction of chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into the equipment) (see Section 4.3)
- $F_{\text{photo\_wafer}}$ = Mass fraction of the photoresist chemical applied that adheres to the wafer surface (kg chemical adhered/kg chemical applied onto the spinning wafer) (see Section 4.4)
- $F_{\text{photo\_develop}}$ = Mass fraction of photoresist chemical removed in development (default = 0.5 kg chemical released/kg chemical adhered to wafer surface) [CSM, 2002]

4.6 Residual Photoresist Contained in Waste Etching and Stripping Solutions Released to Water (Release 5)

Etching the wafer and applying the stripping solution removes the remainder of the photoresist from the wafer after the developing process. Etching solution is used to selectively remove metal from the wafer, and will also contain the film removed from the wafer, including photoresist. Stripping solution can remove the remainder of the photoresist not previously removed. Etching and stripping solutions containing spent photoresist that contain the chemical of interest are typically released to waste water treatment or recycle [SIA, 2003].

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[1] German industry comment to the September 2002 draft ESD states: "[O]nly 4% of the photoresist remains on the wafer. After irradiation, about 2% is polymerized and 2% is not developed and removed by a solvent." These wastes are sent to on-site waste water treatment prior to discharge [UBA Germany, 2003].

The daily release rate of the photoresist chemical of interest (kg/site-day) contained in the waste etching and stripping solutions can be calculated using the following equation:

$$\mathrm{Elocal}_{\mathrm{etch\_strip\_disp}} = \mathrm{Q}_{\mathrm{chem\_day}} \times \left(1 - \mathrm{F}_{\mathrm{equip\_disp}}\right) \times \mathrm{F}_{\mathrm{photo\_wafer}} \times \left(1 - \mathrm{F}_{\mathrm{photo\_develop}}\right) \qquad (4\text{-}5)$$

This release will occur over [$\mathrm{TIME}_{\mathrm{apply\_days}}$] days/year from [$\mathrm{N}_{\mathrm{sites}}$] sites.

Where:

- $\mathrm{Elocal}_{\mathrm{etch\_strip\_disposal}}$ = Daily release of chemical of interest (kg chemical released/site-day)
- $\mathrm{Q}_{\mathrm{chem\_day}}$ = Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4)
- $\mathrm{F}_{\mathrm{equip\_disp}}$ = Mass fraction of chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into the equipment) (see Section 4.3)
- $\mathrm{F}_{\mathrm{photo\_wafer}}$ = Mass fraction of the photoresist chemical applied that adheres to the wafer surface (kg chemical adhered/kg chemical applied onto the spinning wafer) (see Section 4.4)
- $\mathrm{F}_{\mathrm{photo\_develop}}$ = Mass fraction of photoresist chemical removed in development (kg chemical released/kg chemical adhered to wafer surface) (see Section 4.5)

5 OCCUPATIONAL EXPOSURE ASSESSMENTS

The following section presents estimation methods for occupational exposures to nonvolatile chemicals used within photoresists to manufacture semiconductors. Figures 2-2a and 2-2b illustrate the occupational activities performed within the semiconductor manufacturing process that have the greatest potential for occupational exposure to a nonvolatile photoresist chemical.

EPA obtained detailed descriptions of these activities through contacts with the U.S. Semiconductor Industry Association (SIA) and other individuals with working experience within the semiconductor manufacturing industry. In addition, EPA obtained the total number of workers employed by the semiconductor manufacturing industry from recent U.S. Census Bureau data.

EPA did not find industry-specific exposure monitoring data in the references reviewed for this ESD. The concentration of photoresist expected to be contained in the captured waste solvents (e.g., developer, etching, and stripping) has also not been found to date. Section 8 lists the sources reviewed and includes full citations for those specifically used in these calculations. Appendix C contains additional sources relevant to this the subject but not specifically cited.

The occupational exposure estimates presented in this document are based on standard EPA conservative, screening-level dermal exposure models. Table 5-1 summarizes the exposure estimation methods used in this ESD. Note that the standard model default values cited are current as of the date of this ESD; however, EPA may update these models as additional data become available and recommends that the most current version of the models be used in these calculations.

Inhalation exposures to the nonvolatile photoresist chemical are generally not expected. While some misting may occur during the spin-coat application of the photoresist, this process is conducted within an enclosed apparatus; therefore, worker exposure to the mist is not expected during routine operations. In addition, small amounts of the photoresist may volatilize and be removed during dry/plasma etching and stripping of the wafer surfaces; however, the amount of photoresist in these exhausts are expected to be negligible and no inhalation exposures are expected [Shah, 2006].

EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Appendix B provides additional information on ChemSTEER, including information on obtaining the program, as well as background information, model equations, and default values for all standard EPA models.

Table 5-1. Summary of Photoresist Use Scenario Exposure Models

Exposure Activity	Description	Route of Exposure/ Physical Form	Worker Type	Model Name or Description[a]	Standard EPA Model (✓)
A	Change-out of liquid photoresist containers	Dermal exposure to liquid chemical	Operator	EPA/OPPT 1-Hand Dermal Contact with Liquid Model	✓
B	Exposure to liquid photoresist during empty container cleaning and/or disposal	Dermal exposure to liquid chemical	Technician	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	✓
C	Exposure to liquid photoresist during routine equipment cleaning/maintenance	Dermal exposure to liquid chemical	Technician	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	✓
D	Change-out of excess (spun-off) photoresist collection container(s)	Dermal exposure to liquid chemical	Technician	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	✓
E	Exposure to residual photoresist contained in waste solvent (e.g., developer, etching, stripping) during change-out of collection container(s)	Dermal exposure to liquid chemical	Technician	EPA/OPPT 2-Hand Dermal Contact with Liquid Model	✓

OPPT – EPA's Office of Pollution Prevention and Toxics.
a – Appendix B to this ESD contains additional detailed descriptions for each of the models presented in this section.

5.1 Personal Protective Equipment

Because the wafer surface and all materials used to manufacture the semiconductor must be kept free of dust and other contaminants for the product to function, most manufacturing facilities use cleanrooms where workers are required to wear various PPE. The methods that prevent the worker from contaminating the cleanroom and the product also protect the worker from exposure to the photoresist and other chemicals used in the process.

Most newer or updated semiconductor manufacturing facilities require workers to wear full-body coveralls (i.e., "space suits"), respirators, face shields, and gloves inside the production areas including the utility areas where photoresist supply containers and waste disposal lines are connected to the equipment. As a result, dermal exposures are minimized in these newer facilities. In contrast, older manufacturing facilities, which produce older technology chips, may not require "space suits" and thus, potential dermal exposures may be higher.

As described in Section 2.5, much of the semiconductor manufacturing process is conducted within a closed system, which limits worker exposure to the photoresist chemicals. Some sites have separate work areas outside the wafer processing area (e.g., "chemical kitchens") in which the photoresist and other chemical containers and supply lines are connected [CEB, 2001b]. Wafers are often manipulated robotically within the closed system, or transferred within “micro” enclosures between process steps. In older facilities, small cassettes of wafers may be manually carried between process steps. While these older cassettes are open, they are within the cleanroom and the workers handling the cassette are required to wear gloves and other PPE that would prevent contamination of the wafer surface, as well as prevent exposure to the photoresist [SIA, 2006].

During nonroutine equipment failure or other situations where the coated wafer surface becomes contaminated, workers may manually remove the wafers from the equipment and transfer them to reprocessing, where the photoresist is stripped from the surface. The cleaned wafers are then returned to the photolithography process for recoating and reexposure [SIA, 2006].

The activities during which workers have the greatest potential to be exposed to photoresist chemicals are those generally performed outside of the closed manufacturing process. These external activities include: disconnecting/connecting photoresist bottles to the application equipment (sometimes performed in a chemical kitchen); handling/cleaning empty bottles (also may be performed in a separate area); handling excess (spun-off) photoresist and other process solvents; and performing routine equipment cleaning and maintenance activities.

Operators and maintenance workers wear solvent-resistant gloves, aprons, face shields, and/or goggles. If workers handle the photoresist bottles and other chemical containers in a separate area, such as the chemical kitchen, they will also likely be wearing respirators with organic vapor cartridges [CEB, 2001b]. Within the wafer processing area, when the level of organic vapors that may be present during nonroutine wafer reprocessing, equipment maintenance or repair is not known, workers may wear full-face or half-face respirators in addition to the standard skin and face protection listed above [SIA, 2006]. As discussed in Section 2.4, EPA has received no additional information to date regarding these nonroutine activities. For the purposes of this ESD, EPA assumes that the nonroutine exposures are rare to the point of being negligible.

5.2 Number of Workers Exposed Per Site

According to the *2004 County Business Patterns* (CBP) for NAICS code 334413 (i.e., Semiconductor and Related Device Manufacturing), an average of 148 workers are employed at each facility [USCB, 2004a]; however, not all are expected to work in the production areas. The *2004 Annual Survey of Manufacturers* (ASM) estimates that approximately 50 percent of the workers within this NAICS code are *production* workers [USCB, 2004b], which are defined by the U.S. Census Bureau to include…

> *…workers (up through the line-supervisor level) engaged in fabricating, processing, assembling, inspecting, receiving, storing, handling, packing, warehousing, shipping (but not delivering), maintenance, repair, janitorial and guard services, product development, auxiliary production for plant’s own use (e.g., power plant), record keeping, and other services closely associated with these production operations at the establishment* [USCB, 2004b].

All other "nonproduction" employees include…

> *…those engaged in supervision above the line-supervisor level, sales (including driver-salespersons), sales delivery (highway truck drivers and their helpers), advertising, credit, collection, installation and servicing of own products, clerical and routine office functions, executive, purchasing, financing, legal, personnel (including cafeteria, medical, etc.), professional, technical employees, and employees on the payroll of the manufacturing establishment engaged in the construction of major additions or alterations utilized as a separate work force* [USCB, 2004b].

In addition, a typical semiconductor facility operates between 6 and 11 major processes, with photolithography being the largest [Shah, 2006]. Therefore, it is likely that only a portion of the production workers described by the U.S. Census data are involved with the photolithography process and are potentially exposed to the photoresist chemical of interest.

However, according to SIA, because these establishments include design centers, sales offices, and warehouses as well as chip manufacturing facilities, and because "it is unlikely that any facility with less than 50 employees could support semiconductor manufacturing," those establishments with less than 50 employees should not be considered when determining the total number of chip manufacturing establishments [SIA, 2003]. The average U.S. Census data support this assumption.

Note that based on a visit to a semiconductor manufacturing facility, EPA previously estimated that an average of 20 to 25 workers per facility routinely handle the photoresist chemicals and therefore may be exposed [CEB, 2001a]. EPA revised this estimate using more recent information obtained through contacts with SIA and individuals with working experience in the semiconductor manufacturing industry to estimate the number of equipment operators and maintenance/waste management technicians that may be exposed to photoresist chemicals. The following subsections summarize additional information regarding the numbers of operators and technicians that are assumed in this ESD to routinely handle photoresist chemicals, as well as the specific exposure activities expected to be performed by each. This estimate is within the range of data found in the U.S. Census Bureau's CBP and ASM.

5.2.1 Equipment Operators

SIA estimates that these facilities may operate between two and eight spin-coating lines and may run between 30 and 50 etch tools on a continuous, 24-hour basis [SIA, 2006]. Thus, EPA assumed that each site operates three shifts of workers per day. Another contact estimated that large plants may operate between 8 and 12 production lines and each manufacturing line would use two operators per shift [Spinillo, 2005]. SIA estimates that 25 to150 operators work at each site over all shifts [SIA, 2006].

Equipment operators change out the photoresist containers once per shift (Exposure A) [Spinillo, 2005], as well as routinely transfer coated wafers between equipment enclosures as necessary [SIA, 2006]. Operators' greatest potential for exposure to photoresists occurs during the bottle change-out; therefore, this ESD focuses on exposure assessment to the spin-coat line operators, as opposed to the etch tool operators.

In the absence of site-specific information, two operators may be assumed to work each spin-coating line on each shift [Spinillo, 2005]. Additionally, each site may be assumed to operate up to eight spin-coating lines over three eight-hour shifts per day (as listed above, the greatest potential for operator exposure to photoresist is along the spin-coating line, not the etching line). Therefore, the following equation may be used to estimate the number of operators potentially exposed to the photoresist:

$$N_{operators\_site\_day} = N_{operators\_line\_shift} \times N_{lines\_site} \times N_{shifts\_day} \quad (5\text{-}1)$$

Where:

- $N_{operators\_site\_day}$ = Total number of equipment operators handling photoresist per site, per day (workers/site-day)
- $N_{operators\_line\_shift}$ = Number of equipment operators handling photoresist per production line, per shift (default: 2 workers/line-shift [Spinillo, 2005])
- N_{lines_site} = Number of production lines resulting in operator photoresist exposure (i.e., spin-coating lines) per site (default: 8 spin-coating lines per site (high-end) [SIA, 2006] [Spinillo, 2005])
- N_{shifts_day}= Number of working shifts per day (default: 3 shifts/day, [SIA, 2006])

5.2.2 Equipment Maintenance/Waste Management Technicians

One contact estimated that a smaller site would use approximately four maintenance/waste management technicians per shift and that a larger site would use between 5 and 12 technicians per shift [Spinillo, 2005]. This is consistent with an estimate provided by the SIA of between 10 and 30 technicians at each site over all shifts [SIA, 2006], which would be the equivalent of 3 to 10 technicians per shift if three shifts per site, per day is assumed.

Maintenance technicians perform regular cleaning and change-out of the waste photoresist (i.e., the excess spin-off photoresist) (Exposure D) and other process solvents (i.e., waste developer, etching, and stripping solutions containing photoresist) that are collected during regular process operations (Exposure E) [Spinillo, 2005]. These technicians are also responsible for regular cleaning, servicing, and repair of the equipment (Exposure C) [SIA, 2006]. EPA recommends assuming that it is these technicians who clean or otherwise handle the empty photoresist containers (Exposure B).

EPA recommends assuming the SIA average of six maintenance/waste management technicians working during each shift at each site. Additionally, each site may be assumed to operate three eight-hour shifts per day. Therefore, the following equation may be used to estimate the number of maintenance/waste management technicians potentially exposed to the photoresist:

$$N_{techs\_site\_day} = N_{techs\_shift} \times N_{shifts\_day} \quad (5\text{-}2)$$

Where:

- $N_{techs\_site\_day}$ = Total number of equipment maintenance/waste management technicians potentially handling photoresist per site, per day (workers/site-day)

- N_{techs_shift} = Number of equipment maintenance/waste management technicians potentially handling photoresist per shift (default: 6 workers/shift (average) [SIA, 2006])
- N_{shifts_day}= Number of working shifts per site, per day (default: 3 shifts/site-day, consistent with Equation 5-1 [SIA, 2006])

5.3 Dermal Exposure to Liquid Photoresist During Change-out of Empty Photoresist Containers (Exposure A)

Equipment operators will disconnect empty photoresist containers from and connect a new container to the spin-coat/application equipment once per shift [Spinillo, 2005]. Based on information obtained from industry contacts, these bottles typically have a quick-connect/disconnect device to facilitate their change-out, and are designed to minimize the amount of residual photoresist that remains in the empty bottle [SIA, 2006].

Dermal exposure to the liquid photoresist in the container during this activity is expected to be minimal. If the concentration of the chemical of interest in the photoresist (F_{chem}) is unknown, EPA recommends assuming 40 percent concentration as a conservative default, as discussed in Section 3.4. As a default, up to 48 equipment operators per site may be exposed during this activity, per Equation 5-1. Inhalation exposure is expected to be negligible for nonvolatile chemicals within liquid photoresists during this activity.

Because the containers are expected to have a quick-connect/disconnect device, thus minimizing dermal exposure, the *EPA/OPPT 1-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during this activity. The rationale, defaults, and limitations of this model are further explained in Appendix B.

The model uses the following equation to estimate potential worker dermal exposure to the chemical of interest in a liquid photoresist for this activity:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \quad (5\text{-}3)$$

This exposure will occur over [the lesser of $N_{cont\_site\_yr}$ (see Section 3.6) or $TIME_{apply\_days}$, up to 250] days per year.

Where:

- EXP_{dermal} = Potential dermal exposure to the chemical of interest per day (mg chemical/day)
- Q_{liquid_skin} = Quantity of liquid photoresist remaining on skin (Defaults: 2.1 mg photoresist/cm^2-incident (high-end) and 0.7 mg photoresist/cm^2-incident (low-end) for routine or incidental contact [CEB, 2000])
- $AREA_{surface}$ = Surface area of contact (default: 420 cm^2 for 1 hand [CEB, 2000])

- $N_{exp\_incident}$[1] = Number of exposure incidents per day (default: 1 incident/day)
- F_{chem} =Mass fraction of the chemical of interest in the photoresist (mg chemical/mg photoresist) (see Section 3.4)

Note that the exposure days per site, per year should be consistent with the process operating days; EPA recommends a maximum of 250 days per year for each employee. This exposure duration maximum default is based on full-time employment and considers an individual worker's vacation, sick, and weekend time (i.e., a 40-hour work week over 50 weeks per year).

5.4 Dermal Exposure to Liquid Photoresist During Cleaning/Handling Empty Photoresist Containers (Exposure B)

Equipment maintenance/waste management technicians routinely collect the empty photoresist containers and potentially rinse the residues from the containers prior to their disposal or shipment to an off-site recycling facility [Shah, 2005]. At some facilities, the empty bottles are not rinsed at the semiconductor manufacturing plant, but are packaged by the technician (e.g., double-bagging [Spinillo, 2005]) for transfer to an off-site disposal or recycling facility.

To perform a conservative assessment, EPA recommends that the containers are assumed rinsed by the technician at the manufacturing site (consistent with the release assessment described in Section 4.2). Dermal exposure to the liquid photoresist in the bottle is expected to occur during this activity. If the concentration of the chemical of interest in the photoresist (F_{chem}) is unknown, EPA recommends assuming 40 percent concentration as a conservative default, as discussed in Section 3.4. As a default, up to 18 equipment maintenance/waste management technicians per site may be exposed during this activity, per Equation 5-2. Inhalation exposure is expected to be negligible for nonvolatile chemicals within liquid photoresists during this activity.

The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during this activity, based on EPA's standard practice for estimating dermal exposures during empty container cleaning activities. The rationale, defaults, and limitations of this model are further explained in Appendix B.

The model uses the following equation to estimate potential worker dermal exposure to the chemical of interest in a liquid photoresist for this activity:

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[1] EPA assumes only one contact per day ($N_{exp\_incident}$ = 1 event/worker-day) because Q_{liquid_skin}, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from the skin or by the skin having repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \quad (5\text{-}4)$$

This exposure will occur over [the lesser of $N_{cont\_site\_yr}$ or $TIME_{apply\_days}$ (consistent with Section 4.2), up to 250] days per year.

Where:

- EXP_{dermal} = Potential dermal exposure to the chemical of interest per day (mg chemical/day)
- Q_{liquid_skin} = Quantity of liquid photoresist remaining on skin (Defaults: 2.1 mg photoresist/cm^2-incident (high-end) and 0.7 mg photoresist/cm^2-incident (low-end) for routine or incidental contact [CEB, 2000])
- $AREA_{surface}$ = Surface area of contact (default: 840 cm^2 for 2 hands [CEB, 2000])
- $N_{exp\_incident}$ = Number of exposure incidents per day (default: 1 incident/day) (see Section 5.3)
- F_{chem} =Mass fraction of the chemical of interest in the photoresist (mg chemical/mg photoresist) (see Section 3.4)

Note that the exposure days per site, per year should be consistent with the release days, but EPA recommends a maximum of 250 days per year for each employee, as discussed in Section 5.3.

5.5 Dermal Exposure to Residual Photoresist During Routine Equipment Cleaning/Maintenance (Exposure C)

Equipment maintenance/waste management technicians routinely clean the spin-coating and etching tools, as well as maintain the equipment. The technician's greatest potential for exposure to residual photoresist is during cleaning of the spin-coating apparatus, which contains excess (spun-off) photoresist that adhered to the walls of the device. In addition, the photoresist supply line filters also contain residual photoresist when changed out. While the frequency of cleaning/maintenance activities is highly site-specific [SIA, 2006], one contact estimated that the spin-coating equipment is cleaned at least monthly, and more often if the photoresist formulation is thicker (e.g., biweekly or weekly), and that the supply line filters are changed out annually [Spinillo, 2005]. Another source estimated that the equipment is cleaned weekly or daily, and the supply line filters changed out between 6 and 12 times per year [Shah, 2006]. The technician may also come into contact with residual photoresist when cleaning/maintaining other parts of the process line; however, these quantities are expected to be significantly less than those encountered in the spin-coat apparatus.

To perform a conservative assessment, EPA recommends assuming that technicians perform equipment cleaning/maintenance daily, which results in dermal exposure to residual photoresist coating the walls, filter, and other parts. If the concentration of the chemical of interest in the photoresist (F_{chem}) is unknown, EPA recommends assuming 40 percent concentration as a conservative default, as discussed in Section 3.4. As a default, up to 18 equipment maintenance/waste management technicians per site may be exposed during this activity, per Equation 5-2. Inhalation exposure is expected to be negligible for nonvolatile chemicals within liquid photoresists during this activity.

The *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during this activity, based on EPA's standard practice for estimating dermal exposures during process equipment cleaning activities. The rationale, defaults, and limitations of this model are further explained in Appendix B.

The model uses the following equation to estimate potential worker dermal exposure to the chemical of interest in a liquid photoresist for this activity:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \qquad (5\text{-}5)$$

This exposure will occur over [the number of cleanings per year (consistent with Section 4.3), up to 250] days per year.

Where:

- EXP_{dermal} = Potential dermal exposure to the chemical of interest per day (mg chemical/day)
- Q_{liquid_skin} = Quantity of liquid photoresist remaining on skin (defaults: 2.1 mg photoresist/cm^2-incident (high-end) and 0.7 mg photoresist/cm^2-incident (low-end) for routine or incidental contact [CEB, 2000])
- $AREA_{surface}$ = Surface area of contact (default: 840 cm^2 for 2 hands [CEB, 2000])
- $N_{exp\_incident}$ = Number of exposure incidents per day (default: 1 incident/day) (see Section 5.3)
- F_{chem} =Mass fraction of the chemical of interest in the photoresist (mg chemical/mg photoresist) (see Section 3.4)

Note that the exposure days per site, per year should be consistent with the number of cleanings per year, but EPA recommends a maximum of 250 days per year for each employee, as discussed in Section 5.3.

5.6 Dermal Exposure to Liquid Photoresist During Change-out of Excess (Spun-off) Photoresist Collection Containers (Exposure D)

Equipment maintenance/waste management technicians routinely disconnect the excess (spun-off) photoresist collection containers from the spin-coating equipment and prepare them for transfer to an off-site solvent reclaimer or other appropriate disposal facility. EPA expects that most facilities use a closed, piped system to collect the excess photoresist and transfer it to the container (drum or bulk tank) [SIA, 2006].

To perform a conservative assessment, EPA recommends that technicians are assumed to routinely disconnect excess photoresist containers from the equipment, which would potentially result in dermal exposure to the photoresist remaining in the transfer line. If the concentration of the chemical of interest in the photoresist (F_{chem}) is unknown, EPA recommends assuming 40 percent concentration as a conservative default, as discussed in Section 3.4. As a default, up to 18 equipment maintenance/waste management technicians per site may be exposed during this activity, per Equation 5-2. Inhalation exposure is expected to be negligible for nonvolatile chemicals within liquid photoresists during this activity.

Because the excess photoresist collection system is expected to be closed, except for routine disconnection/change-out of the containers, the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* may be used to estimate dermal exposure to the chemical of interest in a liquid formulation during this activity. The rationale, defaults, and limitations of this model are further explained in Appendix B.

The model uses the following equation to estimate potential worker dermal exposure to the chemical of interest in a liquid photoresist for this activity:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \qquad (5\text{-}6)$$

This exposure will occur over [the lesser of $TIME_{apply\_days}$ (consistent with Section 4.4) or 250] days per year.

Where:

- EXP_{dermal} = Potential dermal exposure to the chemical of interest per day (mg chemical/day)
- Q_{liquid_skin} = Quantity of liquid photoresist remaining on skin (defaults: 2.1 mg photoresist/cm^2-incident (high-end) and 0.7 mg photoresist/cm^2-incident (low-end) for routine or incidental contact [CEB, 2000])
- $AREA_{surface}$ = Surface area of contact (default: 840 cm^2 for 2 hands [CEB, 2000])
- $N_{exp\_incident}$ = Number of exposure incidents per day (default: 1 incident/day) (see Section 5.3)
- F_{chem} =Mass fraction of the chemical of interest in the photoresist (mg chemical/mg photoresist) (see Section 3.4)

Note that the exposure days per site, per year should be consistent with the process operating days, but EPA recommends a maximum of 250 days per year for each employee, as discussed in Section 5.3.

5.7 Dermal Exposure to Residual Photoresist During Change-out of Waste Solvent Collection Containers (Exposure E)

Equipment maintenance/waste management technicians routinely disconnect the waste solvent collection containers from the semiconductor manufacturing equipment during changeout. The waste solvents in these containers include developer, etchant, and stripper containing residual photoresist chemicals that were removed from the wafer surface. The workers may prepare these waste solvent containers for transfer to an off-site solvent reclaimer or other appropriate disposal facility. Some facilities may alternatively pipe the waste solvents to a bulk storage tank, where they are subsequently transferred to a tank truck for transport to the disposal facility or reclaimer [SIA, 2006].

EPA expects, however, that most facilities use a closed, piped system to collect the waste solvents and transfer them to an on-site wastewater treatment system (WWTS) and/or to a publicly owned treatment works (POTW) [SIA, 2006] [McCoy, 2005]. EPA estimates the technicians' exposure to the waste solvents from the process to be single exposure activity, as it assumes that all process solvents are generally collected via a single collection system.

To perform a conservative assessment, EPA recommends that technicians are assumed to routinely disconnect waste solvent containers from the equipment, which would potentially result in dermal exposure to residual amounts of waste solvent remaining in the transfer line that contains residual amounts of photoresist removed from the wafer surface. If the concentration of the chemical of interest in the photoresist (F_{chem}) is unknown, EPA recommends assuming 40 percent concentration as a conservative default, as discussed in Section 3.4. As a default, up to 18 equipment maintenance/waste management technicians per site may be exposed during this activity, per Equation 5-2. Inhalation exposure is expected to be negligible for nonvolatile chemicals within liquid photoresists during this activity.

To date, EPA has found no information about the concentration of photoresist that is expected to be contained in the waste solvent (F_{photo_waste}). While the photoresist chemical became more concentrated on the wafer surface following the "soft bake" and "hard bake" processes (i.e., removal of the solvent portion), the remaining chemical removed from the wafer surface is expected to be diluted by the waste developer, etching, and stripping solvents. If site-specific information is not available, EPA recommends assuming that the remaining photoresist that is removed from the wafer surface is effectively diluted 100 times within the waste solvent, based on engineering judgment (i.e., F_{photo_waste} = 0.01 mg photoresist/mg waste solvent).

Because the excess photoresist collection system is expected to be closed, except for routine disconnection/change-out of the containers, EPA recommends using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model* to estimate dermal exposure to the chemical of interest in a liquid formulation during this activity. The rationale, defaults, and limitations of this model are further explained in Appendix B.

The model uses the following equation to estimate potential worker dermal exposure to the chemical of interest in a liquid photoresist for this activity:

$$EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \times F_{photo\_waste} \quad (5\text{-}7)$$

This exposure will occur over [the lesser of $TIME_{apply\_days}$ (consistent with Sections 4.5 and 4.6) or 250] days per year.

Where:

- EXP_{dermal} = Potential dermal exposure to the chemical of interest per day (mg chemical/day)
- Q_{liquid_skin} = Quantity of liquid photoresist remaining on skin (defaults: 2.1 mg photoresist/cm^2-incident (high-end) and 0.7 mg photoresist/cm^2-incident (low-end) for routine or incidental contact [CEB, 2000])
- $AREA_{surface}$ = Surface area of contact (default: 840 cm^2 for 2 hands [CEB, 2000])
- $N_{exp\_incident}$ = Number of exposure incidents per day (default: 1 incident/day) (see Section 5.3)

- F_{chem} =Mass fraction of the chemical of interest in the photoresist (mg chemical/mg photoresist) (see Section 3.4)
- F_{photo_waste} = Mass fraction of the photoresist contained in the collected waste solvent (default: = 0.01 mg photoresist/mg waste solvent)

Note that the exposure days per site, per year should be consistent with the process operating days, but EPA recommends a maximum of 250 days per year for each employee, as discussed in Section 5.3.

5.8 Dermal Exposure to Photoresist Coating the Wafer During Nonroutine Transfer of Contaminated Wafers

In general, equipment operators or technicians will not come into direct contact with the photoresist, because of the protections taken to maintain the highest level of purity during the wafer coating process. One exception to this may be during nonroutine equipment failure or other events where the wafer surface becomes contaminated. Operators or technicians may be required to manually remove the coated wafers from the equipment and manually transfer them to reprocessing (i.e., stripping).

EPA has found no data to date with which to quantify the extent of this exposure. Nevertheless, workers are expected to wear appropriate PPE, as described in Section 5.1, which will likely mitigate the potential exposure during these nonroutine events. For this assessment, EPA recommends assuming that nonroutine manual handling of coated wafers is rare to the point of being negligible.

6 SAMPLE CALCULATIONS

This section presents an example of how the equations described in Sections 3 through 5 might be used to estimate releases of and exposures to a nonvolatile chemical found in a liquid photoresist used to manufacture semiconductors. The default values used in these calculations are presented in Sections 3, 4, and 5 and should be used only in the absence of site-specific information. The following data are used in this example calculation:

1. Chemical of interest production volume (Q_{chem_yr}) is *5,000 kg chemical/yr.*
2. Chemical of interest is 15 percent by weight in the photoresist formulation (F_{chem}) (nondefault; assumed to be known in this example).

6.1 General Facility Estimates

6.1.1 Daily Use Rate of Photoresist (Q_{photo_day})

No site-specific information or data are known for the Equation 3-1 parameters (i.e., N_{apply}, $TIME_{apply\_hours}$, and Q_{apply}) used to estimate the daily dispense (or *use*) rate for the photoresist (Q_{photo_day}); therefore, using the default values is appropriate (large-scale semiconductor manufacturing from Table 3-2):

$$Q_{photo\_day} = N_{apply} \times TIME_{apply\_hours} \times \left(\frac{Q_{apply}}{1{,}000\ \text{mL/L}} \right) \times RHO_{photo} \qquad \text{[Eqn. 3-1]}$$

$$Q_{photo\_day} = \frac{1{,}000\ \text{applications}}{\text{site - hr}} \times \frac{24\ \text{hours}}{\text{day}} \times \frac{1.5\ \text{ml photoresist dispensed}}{\text{application}} \times \frac{1\ \text{L}}{1{,}000\ \text{mL}} \times \frac{1\ \text{kg photoresist}}{\text{L}}$$

Q_{photo_day} = 36 kg photoresist dispensed/site-day

6.1.2 Number of Days of Photoresist Application ($TIME_{apply\_days}$)

Since no site-specific information or data are known for the Equation 3-1 parameters (as demonstrated in Section 6.1.1), using the corresponding default value for the number of application days ($TIME_{apply\_days}$) is appropriate (large-scale semiconductor manufacturing from Table 3-2). Assume *360 days/year.*

6.1.3 Daily Use Rate of Chemical of Interest (Q_{chem_day})

$$Q_{chem\_day} = Q_{photo\_day} \times F_{chem} \times \frac{N_{app\_chem}}{N_{app\_phot}} \qquad \text{[Eqn. 3-2]}$$

$$Q_{chem\_day} = \frac{36\ \text{kg photoresist dispensed}}{\text{site - day}} \times \frac{0.15\ \text{kg chemical}}{\text{kg photoresist}} \times \frac{1\ \text{application chemical - containing photoresist}}{\text{application all photoresists}}$$

Q_{chem_day} = 5.4 kg chemical dispensed/site-day

6.1.4 Number of Sites (N_{sites})

$$N_{sites} = \frac{(1 - F_{container\_disp}) \times Q_{chem\_yr}}{Q_{chem\_day} \times TIME_{apply\_days}} \qquad \text{[Eqn. 3-3]}$$

$$N_{sites} = \frac{(1 - 0.006)\text{ kg chem dispensed/kg chem pkgd \& sold} \times 5{,}000\text{ kg chem pkgd \& sold/yr}}{5.4\text{ kg chem dispensed/site - day} \times 360\text{ days/yr}}$$

N_{sites} = 2.6 sites

Round N_{sites} up to the next integer (*3 manufacturing sites*) and recalculate Q_{chem_day}:

$$Q_{chem\_day} = \frac{(1 - 0.006)\text{ kg chem dispensed/kg chem pkgd \& sold} \times 5{,}000\text{ kg chem pkgd \& sold/yr}}{3\text{ sites} \times 360\text{ days/yr}}$$

Q_{chem_day} = 4.60 kg chemical dispensed/site-day

6.1.5 Annual Number of Photoresist Containers Emptied per Site ($N_{cont\_site\_yr}$)

EPA assumes that the photoresist (which is 15% chemical of interest) is shipped to the semiconductor manufacturer in 1-gallon (3.8-liter) bottles, as a default. A density of 1 kg/L is also assumed for the photoresist. The mass capacity for each of the bottles is calculated as:

$$Q_{cont} = V_{cont} \times RHO_{photo} = \frac{3.8\text{ L photoresist}}{\text{container}} \times \frac{1\text{ kg photoresist}}{\text{L}} = 3.8\text{ kg photoresist/container}$$

The number of containers that are emptied per site, per year is therefore calculated as:

$$N_{cont\_site\_yr} = \frac{Q_{chem\_yr}}{F_{chem} \times Q_{cont} \times N_{sites}} \qquad \text{[Eqn. 3-4]}$$

$$N_{cont\_site\_yr} = \frac{5{,}000\text{ kg chem pkgd \& sold/yr}}{0.15\text{ kg chem/kg photoresist} \times 3.8\text{ kg photoresist/container} \times 3\text{ sites}}$$

$N_{cont\_site\_yr}$ = 2,924 containers/site-yr

6.2 Release Assessments

6.2.1 Container Residues Released to Water, Incineration, or Landfill (Release 1)

Since $N_{cont\_site\_yr}$ is greater than $TIME_{apply\_days}$, EPA assumes that more than one container is emptied on each application day. First, the total daily amount of chemical that is received per site (prior to dispensing) (i.e., the amount "packaged and sold" per site-day) is estimated, using the daily use rate for the chemical and applying the fraction of chemical that will remain in the container. Since it is known that the photoresist is in a liquid form and the container is assumed to be a 1-gallon bottle, by default, the *EPA/OPPT Small Container Residual Model* is used to estimate this release. The default fraction of liquid chemical that remains in the empty bottle ($F_{container\_disp}$) is 0.006 kg chemical remaining/kg chemical in full container (see Table B-3 in Appendix B):

$$Q_{chem\_received\_day} = \frac{Q_{chem\_day}}{1 - F_{container\_disp}} = \frac{4.60 \text{ kg chem dispensed/ site} - \text{day}}{(1 - 0.006) \text{kg chem dispensed/ kg chem pkgd \& sold}}$$

$Q_{chem\_received\_day}$ = 4.63 kg chem. pkgd & sold/site-day (i.e., daily amount received)

The following equation is then used to estimate the daily release of chemical via the rinsing/disposal of the waste containers:

$$\text{Elocal}_{container\_residue\_disp} = Q_{chem\_received\_day} \times F_{container\_disp} \qquad \text{[Eqn. 4-1b]}$$

$$\text{Elocal}_{container\_residue\_disp} = \frac{4.63 \text{ kg chem received}}{\text{site - day}} \times \frac{0.006 \text{ kg chem remaining in container and released}}{\text{kg chem received in full container}}$$

$\text{Elocal}_{container\_residue\_disp}$ = 0.0278 kg chem. released/site-day
…over 360 days/year from 3 sites

6.2.2 Equipment Cleaning Residues Released to Incineration or Landfill

$$\text{Elocal}_{equip\_disp} = Q_{chem\_day} \times F_{equip\_disp} \qquad \text{[Eqn. 4-2]}$$

$$\text{Elocal}_{equip\_disp} = 4.60 \frac{\text{kg chem dispensed}}{\text{site - day}} \times 0.01 \frac{\text{kg residual chem released from equipment cleaning}}{\text{kg chem dispensed}}$$

$\text{Elocal}_{equip\_disp}$ = 0.046 kg chem. released/site-day
…over 360 days/year from 3 sites

6.2.3 Excess Photoresist (Spin-off) Released to Incineration (Release 3)

$$\text{Elocal}_{excess\_disp} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times (1 - F_{photo\_wafer}) \qquad \text{[Eqn. 4-3]}$$

$$\text{Elocal}_{excess\_disp} = \frac{4.60 \text{ kg chem dispensed}}{\text{site} - \text{day}} \times \frac{(1 - 0.01) \text{kg chem applied to wafer}}{\text{kg chem dispensed}} \times \frac{(1 - (0.01 \text{ to } 0.07)) \text{kg chem not adhered}}{\text{kg chem applied}}$$

$\text{Elocal}_{excess\_disp}$ = 4.2-4.5 kg excess chem. released/site-day
…over 360 days/year from 3 sites

6.2.4 Residual Photoresist Contained in Waste Developer Solution Released to Water (Release 4)

$$\text{Elocal}_{developer} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times F_{photo\_wafer} \times F_{photo\_develop} \qquad \text{[Eqn. 4-4]}$$

$$\text{Elocal}_{\text{developer}} = \frac{4.60\text{ kg chem dispensed}}{\text{site} - \text{day}} \times \frac{(1 - 0.01)\text{ kg chem applied to wafer}}{\text{kg chem dispensed}} \times \frac{(0.01\text{ to }0.07)\text{ kg chem adhered}}{\text{kg chem applied}} \times \frac{0.5\text{ kg chem released}}{\text{kg chem adhered}}$$

$\text{Elocal}_{\text{developer}}$ = 0.023-0.16 kg chem. released/site-day
…over 360 days/year from 3 sites

6.2.5 Residual Photoresist Contained in Spent Etching and Stripper Solutions (Release 5)

$$\text{Elocal}_{\text{etch\_strip\_disp}} = Q_{\text{chem\_day}} \times (1 - F_{\text{equip\_disp}}) \times F_{\text{photo\_wafer}} \times (1 - F_{\text{photo\_develop}}) \qquad \text{[Eqn. 4-5]}$$

$$\text{Elocal}_{\text{etch\_strip\_disp}} = \frac{4.60\text{ kg chem dispensed}}{\text{site} - \text{day}} \times \frac{(1 - 0.01)\text{ kg chem applied to wafer}}{\text{kg chem dispensed}} \times \frac{(0.01\text{ to }0.07)\text{ kg chem adhered}}{\text{kg chem applied}} \times \frac{(1 - 0.5)\text{ kg chem released}}{\text{kg chem adhered}}$$

$\text{Elocal}_{\text{developer}}$ = 0.023-0.16 kg chem. released/site-day
…over 360 days/year from 3 sites

6.3 Occupational Exposure Assessments

6.3.1 Number of Equipment Operators per Site

$$N_{\text{operators\_site\_day}} = N_{\text{operators\_line\_shift}} \times N_{\text{lines\_site}} \times N_{\text{shifts\_day}} \qquad \text{[Eqn 5-1]}$$

$$N_{\text{operators\_site\_day}} = \frac{2\text{ operators}}{\text{line - shift}} \times \frac{8\text{ lines}}{\text{site}} \times \frac{3\text{ shifts}}{\text{day}}$$

$N_{\text{operators\_site\_day}}$ = 48 operators/site-day

6.3.2 Number of Equipment Maintenance/Waste Management Technicians per Site

$$N_{\text{techs\_site\_day}} = N_{\text{techs\_shift}} \times N_{\text{shifts\_day}} \qquad \text{[Eqn. 5-2]}$$

$$N_{\text{techs\_site\_day}} = \frac{6\text{ technicians}}{\text{shift}} \times \frac{3\text{ shifts}}{\text{site - day}}$$

$N_{\text{techs\_site\_day}}$ = 18 technicians/site-day

6.3.3 Dermal Exposure to Liquid Photoresist During Change-out of Empty Photoresist Containers (Operators) (Exposure A)

The potential operator exposure to the chemical within the liquid photoresist is calculated using the *EPA/OPPT 1-Hand Dermal Contact with Liquid Model*:

$$\mathrm{EXP}_{\mathrm{dermal}} = \mathrm{Q}_{\mathrm{liquid\_skin}} \times \mathrm{AREA}_{\mathrm{surface}} \times \mathrm{N}_{\mathrm{exp\_incident}} \times \mathrm{F}_{\mathrm{chem}} \qquad \text{[Eqn. 5-3]}$$

$$= \left[\frac{0.7 \text{ to } 2.1\,\text{mg photoresist}}{\text{cm}^2 - \text{incident}}\right] \times 420\,\text{cm}^2 \times \frac{1\,\text{incident}}{\text{day}} \times \frac{0.15\,\text{mg chem}}{\text{mg photoresist}}$$

$$\mathrm{EXP}_{\mathrm{dermal}} = \frac{44\text{ - }132\,\text{mg chem.}}{\text{day}}$$

…over 250 days/year

6.3.4 *Dermal Exposure to Liquid Photoresist During Cleaning/Handling Empty Photoresist Containers (Technicians) (Exposure B)*

The potential technician exposure to the chemical within the liquid photoresist is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\mathrm{EXP}_{\mathrm{dermal}} = \mathrm{Q}_{\mathrm{liquid\_skin}} \times \mathrm{AREA}_{\mathrm{surface}} \times \mathrm{N}_{\mathrm{exp\_incident}} \times \mathrm{F}_{\mathrm{chem}} \qquad \text{[Eqn. 5-4]}$$

$$= \left[\frac{0.7 \text{ to } 2.1\,\text{mg photoresist}}{\text{cm}^2\text{ - incident}}\right] \times 840\,\text{cm}^2 \times \frac{1\,\text{incident}}{\text{day}} \times \frac{0.15\,\text{mg chem.}}{\text{mg photoresist}}$$

$$\mathrm{EXP}_{\mathrm{dermal}} = \frac{88 - 265\,\text{mg chem.}}{\text{day}}$$

…over 250 days/year

6.3.5 *Dermal Exposure to Residual Photoresist During Routine Equipment Cleaning/Maintenance (Technicians) (Exposure C)*

The potential technician exposure to the chemical within the liquid photoresist is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\mathrm{EXP}_{\mathrm{dermal}} = \mathrm{Q}_{\mathrm{liquid\_skin}} \times \mathrm{AREA}_{\mathrm{surface}} \times \mathrm{N}_{\mathrm{exp\_incident}} \times \mathrm{F}_{\mathrm{chem}} \qquad \text{[Eqn. 5-5]}$$

$$= \left[\frac{0.7 \text{ to } 2.1\,\text{mg photoresist}}{\text{cm}^2\text{ - incident}}\right] \times 840\,\text{cm}^2 \times \frac{1\,\text{incident}}{\text{day}} \times \frac{0.15\,\text{mg chem.}}{\text{mg photoresist}}$$

$$\mathrm{EXP}_{\mathrm{dermal}} = \frac{88 - 265\,\text{mg chem.}}{\text{day}}$$

…over 250 days/year

6.3.6 *Dermal Exposure to Liquid Photoresist During Change-out of Excess (Spun-off) Photoresist Collection Containers (Technicians) (Exposure D)*

The potential technician exposure to the chemical within the liquid photoresist is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\mathrm{EXP}_{\mathrm{dermal}} = \mathrm{Q}_{\mathrm{liquid\_skin}} \times \mathrm{AREA}_{\mathrm{surface}} \times \mathrm{N}_{\mathrm{exp\_incident}} \times \mathrm{F}_{\mathrm{chem}} \qquad \text{[Eqn. 5-6]}$$

$$= \left[\frac{0.7 \text{ to } 2.1 \text{ mg photoresist}}{\text{cm}^2 \text{ - incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{0.15 \text{ mg chem.}}{\text{mg photoresist}}$$

$$\text{EXP}_{\text{dermal}} = \frac{88 - 265 \text{ mg chem.}}{\text{day}}$$

…over 250 days/year

6.3.7 Dermal Exposure to Residual Photoresist During Change-out of Waste Solvent Collection Containers (Technicians) (Exposure E)

The potential technician exposure to the chemical within the liquid photoresist is calculated using the *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*:

$$\text{EXP}_{\text{dermal}} = \text{Q}_{\text{liquid\_skin}} \times \text{AREA}_{\text{surface}} \times \text{N}_{\text{exp\_incident}} \times \text{F}_{\text{chem}} \times \text{F}_{\text{photo\_waste}} \qquad \text{[Eqn. 5-7]}$$

$$= \left[\frac{0.7 \text{ to } 2.1 \text{ mg photoresist}}{\text{cm}^2 \text{ - incident}} \right] \times 840 \text{ cm}^2 \times \frac{1 \text{ incident}}{\text{day}} \times \frac{0.15 \text{ mg chem}}{\text{mg photoresist}} \times \frac{0.01 \text{ mg photoresist}}{\text{mg waste solution}}$$

$$\text{EXP}_{\text{dermal}} = \frac{0.88 - 2.6 \text{ mg chem.}}{\text{day}}$$

…over 250 days/year

7 DATA GAPS/UNCERTAINTIES AND FUTURE WORK

This ESD relies on anecdotal data and information gathered from various sources to generate general facility estimates, release estimates, and exposure estimates. EPA wishes to make this ESD as detailed and up-to-date as possible, such that the risk-screening assessments reflect current industrial practices. This ESD could be improved by collecting measured data and associated information to verify or supersede the anecdotal data and information.

Reviewers should feel free to provide additional information and data that could further enhance and improve the methods described in this ESD, as well as to recommend additional resources that may be useful to the development of this ESD.

The key data gaps are summarized below. Note that the data gaps are listed in order of importance (the first being most important):

1. EPA found limited information on the concentrations of various chemicals within photoresist formulations. The information presented in this ESD is limited to the relative portions of nonvolatile vs. volatile/solvent chemicals found within typical photoresists. Additional formulation data that could be used to generally demonstrate typical concentrations of the various types of nonvolatile chemicals used in photoresists (e.g., photoactive compounds, base resins, viscosity control agents, dyes) would further enhance the calculations.

2. EPA found no industry-specific information that could be used to quantify the concentration of residual photoresist contained in the waste solvents collected from the process (i.e., developer, etching, and stripping); therefore, this ESD assumes the photoresist is effectively diluted 100 times within the waste solvent based on engineering judgment. Additional information that could be used to estimate these concentrations (including appropriate process monitoring data) would improve this estimate.

3. The ESD assumes that semiconductor manufacturers use a single photoresist formulation/product (containing the chemical of interest) for all wafers that are processed at the site (i.e., $N_{app\_chem}/N_{app\_photo} = 1$) (see Section 3.4). Additional information to validate this assumption would improve the quality of the estimates.

4. EPA found no industry-specific information that could be used to quantify the frequency of nonroutine process failures during which the wafer surfaces become contaminated and must either be discarded or reprocessed. Additional information for estimating the frequency of these failures or portion of wafers that are discarded/reprocessed would enhance the release and exposure estimates.

5. The ESD uses standard EPA estimates to determine the amount of photoresist residue that adheres to the process equipment surfaces (Release 2). Industry-specific loss fractions for photoresist residues that are removed from the equipment during routine maintenance (e.g., parts cleaning, supply line filter change-out and disposal) would further improve these estimates.

8 REFERENCES

The specific information researched in the development of this document include process description, operating information, chemicals used, wastes generated, worker activities, and exposure information. Research for this ESD was primarily conducted during its initial development in the 2001-2003 timeframe. In 2005, EPA conducted additional research specifically focused on information to augment the occupational exposure assessment methods. This additional research primarily included soliciting industry members for their input.

Specific sources investigated in the development of this ESD include documents and data from the following sources:

- U.S. Environmental Protection Agency (EPA);
- U.S. Census Bureau;
- Kirk-Othmer Encyclopedia of Technology;
- U.S. Semiconductor Industry Association (SIA - http://www.sia-online.org) and other individuals with working experience in the semiconductor manufacturing industry;
- Organisation for Economic Co-operation and Development (OECD) member countries (i.e., Canada, Germany, and the Netherlands); and
- International Semiconductor Environmental Safety and Health Conference (ISESH).

The references specifically cited in this ESD are provided below. Appendix D lists other relevant sources of information about photoresist use in semiconductor manufacturing.

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[OECD, 2004a] *Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing*; OECD Series on Emission Scenario Documents; Number 9; ENV/JM/MONO(2004)14; June 24, 2004. Available on line at: http://www.olis.oecd.org/olis/2004doc.nsf/LinkTo/env-jm-mono(2004)14.

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[SIA, 2003] Email from Chuck Fraust of the Semiconductor Industry Association (SIA), to Nhan Nguyen of CEB; *Comments on the Draft Generic Photolithography*

Scenario; 13 August 2003; and subsequent follow-up communications through September 2003.

[SIA, 2005] Teleconference with Chuck Fraust and members of SIA, Greg Macek and Prabodh Shah of CEB, and Leslie Churilla of Eastern Research Group, Inc; *Research for Updating Worker Exposure Assessment Information for the Photoresist Use Generic Scenario*; 7 December 2005.

[SIA, 2006] Email from Chuck Fraust of the Semiconductor Industry Association (SIA), to Greg Macek of CEB; *SIA Response to EPA Request for Information*; 9 March 2006.

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APPENDIX A:
ESTIMATION EQUATION SUMMARY AND DEFAULT PARAMETER VALUES

Summary of Release and Exposure Estimation Equations

Table A-1 summarizes the equations introduced in Sections 3 through 5, which are used to calculate the general facility parameters. Tables A-2 and A-3 summarize the equations used in evaluating releases of and exposures to photoresist chemicals used in the manufacture of semiconductors. Table A-4 summarizes the parameters for each equation, the default value if applicable, and the source. The default values for the ChemSTEER models are presented in Appendix B.

Table A-1. Photoresist Use Scenario Release and Exposure Calculation Summary

General Facility Estimates
Daily Dispense (or Use) Rate of Photoresist Containing the Chemical of Interest per Site (Q_{photo_day}):
$Q_{photo\_day} = N_{apply} \times TIME_{apply\_hours} \times Q_{apply} / 1{,}000\ mL/L \times RHO_{photo}$ (Eqn. 3-1)
Daily Dispense (or Use) Rate of Chemical of Interest Within the Photoresist (Q_{chem_day}):
$Q_{chem\_day} = Q_{photo\_day} \times F_{chem} \times \frac{N_{app\_chem}}{N_{app\_photo}}$ (Eqn. 3-2)
Number of Sites Using Photoresists that Contain the Chemical of Interest (N_{sites}):
$N_{sites} = \frac{(1 - F_{container\_disp}) \times Q_{chem\_yr}}{Q_{chem\_day} \times TIME_{apply\_days}}$ (Eqn. 3-3)
Annual Number of Chemical-Containing Photoresist Containers Emptied per Site ($N_{cont\_site\_yr}$):
$N_{cont\_site\_yr} = \frac{Q_{chem\_yr}}{F_{chem} \times Q_{cont} \times N_{sites}}$ (Eqn. 3-4)

Table A-2. Environmental Release Calculation Summary

Release Calculations		
Source	**Possible Medium**	**Daily Release Rates (kg/site-day), Elocal (for Given Sources)**
Container Residue	Water Landfill Incineration	If $N_{cont\_site\_yr}$ is fewer than $TIME_{apply\_days}$: $Elocal_{container\_residue\_disp} = Q_{cont} \times F_{chem} \times F_{container\_disp} \times N_{cont\_site\_day}$ …released over [$N_{cont\_site\_yr}$] days/year from [N_{sites}] sites (Eqn. 4-1a) If $N_{cont\_site\_yr}$ is greater than $TIME_{apply\_days}$: $Elocal_{container\_residue\_disp} = Q_{chem\_received\_day} \times F_{container\_disp}$ …released over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites (Eqn. 4-1b)
Equipment Cleaning Residue	Landfill Incineration	$Elocal_{equip\_disp} = Q_{chem\_day} \times F_{equip\_disp}$ …released over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites (Eqn. 4-2)
Application Excess (Spin-off)	Incineration	$Elocal_{excess\_disp} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times (1 - F_{photo\_wafer})$ …released over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites (Eqn. 4-3)
Residual in Waste Developer Solution	Water	$Elocal_{developer} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times F_{photo\_wafer} \times F_{photo\_develop}$ …released over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites (Eqn. 4-4)
Residual in Waste Etching and Stripping Solutions	Water	$Elocal_{etch\_strip\_disp} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times F_{photo\_wafer} \times (1 - F_{photo\_develop})$ …released over [$TIME_{apply\_days}$] days/year from [N_{sites}] sites (Eqn. 4-5)

Table A-3. Occupational Exposure Calculation Summary

Occupational Exposure Calculations
Number of Workers Exposed Per Site: Equipment Operators: $N_{operators\_site\_day} = N_{operators\_line\_shift} \times N_{lines\_shift} \times N_{shifts\_day}$ (Eqn. 5-1) Equipment Maintenance/Waste Management Technicians: $N_{techs\ site\ day} = N_{techs\ shift} \times N_{shifts\ day}$ (Eqn. 5-2)
Dermal Exposure to Liquid Photoresist During Change-out of Empty Photoresist Containers: $EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem}$ …over [the lesser of $N_{cont\ site\ yr}$ (see Section 3.6) or $TIME_{apply\ days}$, up to 250] days/year (Eqn. 5-3)
Dermal Exposure to Liquid Photoresist During Cleaning/Handling Empty Photoresist Containers: $EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem}$ …over [the lesser of $N_{cont\ site\ yr}$ or $TIME_{apply\ days}$ (consistent with Section 4.2), up to 250] days/year (Eqn. 5-4)
Dermal Exposure to Residual Photoresist During Routine Equipment Cleaning/Maintenance: $EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem}$ …over [the number of cleanings per year (consistent with Section 4.3), up to 250] days/year (Eqn. 5-5)
Dermal Exposure to Liquid Photoresist During Change-out of Excess (Spun-off) Photoresist Collection Containers: $EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem}$ …over [the lesser of $TIME_{apply\ days}$ (consistent with Section 4.4) or 250] days/year (Eqn. 5-6)
Dermal Exposure to Residual Photoresist During Change-out of Waste Solvent Collection Containers: $EXP_{dermal} = Q_{liquid\_skin} \times AREA_{surface} \times N_{exp\_incident} \times F_{chem} \times F_{photo\_waste}$ …over [the lesser of $TIME_{apply\ days}$ (consistent with Sections 4.5 and 4.6) or 250] days/year (Eqn. 5-7)

Table A-4. Summary of Equation Parameter Default Values Used in the ESD

Variable	Variable Description	Default Value	Data Source
$AREA_{surface}$	Surface area of contact (cm^2)	420 cm^2 (1 hand) 840 cm^2 (2 hands)	CEB, 2000
F_{chem}	Mass fraction of chemical of interest in photoresist (kg chemical/kg photoresist)	0.4 (high-end)	Courtney, 1994
$F_{container\_disp}$	Fraction of photoresist remaining in the container as residue (kg photoresist remaining/kg photoresist in full container)	0.006	CEB, 1992
F_{equip_disp}	Fraction of photoresist chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into equipment)	0.01	CEB, 1992
$F_{photo\_develop}$	Fraction of photoresist chemical removed from the wafer surface during development (kg chemical released/kg chemical adhered to wafer surface)	0.50	CSM, 2002
F_{photo_wafer}	Fraction of photoresist chemical that adheres to the wafer surface (kg chemical adhered/kg chemical applied onto spinning wafer surface)	0.07	SIA, 2003 ISESH, 2002
F_{photo_waste}	Fraction of residual photoresist contained in the waste process solutions (i.e., developer, etching, and stripping)	0.01	EPA assumption
$\frac{N_{app\_chem}}{N_{app\_photo}}$	Fraction of the total number of photoresist applications that contain the chemical of interest	1	EPA assumption
N_{apply}	Number of applications per site, per hour (applications/site-hr)	1,000 (See Table 3-2 for alternate values)	SIA, 2003
$N_{cont\_site\_day}$	Number of containers emptied per site, per day (containers/site-day)	1 (only used if $N_{cont\_site\_yr}$ is less than $TIME_{apply\_days}$)	EPA assumption
$N_{exp\_incident}$	Number of exposure incidents per day (incidents/day)	1	CEB, 2000
N_{lines_site}	Number of production lines resulting in operator photoresist exposure (i.e., spin-coating lines) per site (lines/site)	8 (high-end)	SIA, 2006 Spinillo, 2005
$N_{operators\_line\_shift}$	Number of equipment operators handling photoresist per production line, per shift (workers/line-shift)	2	Spinillo, 2005
N_{shifts_day}	Number of working shifts per day (shifts/day)	3 (24-hour day)	SIA, 2006
N_{techs_shift}	Number of equipment maintenance/waste management technicians potentially handling photoresist per shift, per site (workers/shift-site)	6 (average)	SIA, 2006

Variable	Variable Description	Default Value	Data Source
Q_{apply}	Quantity of photoresist dispensed per wafer application (ml photoresist dispensed/application)	1.5 (See Table 3-2 for alternate values)	SIA, 2003
Q_{liquid_skin}	Quantity of liquid photoresist remaining on skin (mg/cm^2-incident)	2.1 (high-end) 0.7 (low-end)	CEB, 2000
RHO_{photo}	Density of the photoresist (kg/L)	1	EPA assumption
$TIME_{apply\_days}$	Number of days of photoresist application per year (days/yr)	360 (See Table 3-2 for alternate values)	SIA, 2003
$TIME_{apply\_hours}$	Hours of application per day (hr/day)	24 (See Table 3-2 for alternate values)	SIA, 2006 SIA, 2003
V_{cont}	Volume of photoresist per container (L/container)	3.8 (1-gallon bottle)	SIA, 2006

APPENDIX B:
BACKGROUND INFORMATION AND EQUATIONS/DEFAULTS FOR THE STANDARD EPA ENVIRONMENTAL RELEASE AND WORKER EXPOSURE MODELS

B.1 Introduction

This appendix provides background information and a discussion of the equations, variables, and default assumptions for each of the standard release and exposure models used by EPA in estimating environmental releases and worker exposures. The models described in this appendix are organized into the following five sections:

- Section B.2: Chemical Vapor Releases & Associated Inhalation Exposures;
- Section B.3: Container Residue Release Models (non-air);
- Section B.4: Process Equipment Residue Release Models (non-air);
- Section B.5: Chemical Particle Inhalation Exposure Models; and
- Section B.6 : Dermal Exposure Models.

Please refer to the guidance provided in the ESD for estimating environmental releases and worker exposures using these standard models, as it may suggest the use of certain overriding default assumptions to be used in place of those described for each model within this appendix.

This appendix includes a list of the key reference documents that provide the background and rationale for each of the models discussed. These references may be viewed in their entirety through the ChemSTEER Help System. To download and install the latest version of the ChemSTEER software and Help System, please visit the following EPA web site:

http://www.epa.gov/opptintr/exposure/docs/chemsteer.htm

B.2 Chemical Vapor Releases & Associated Inhalation Exposures

This section discusses the models used by EPA to estimate chemical vapor generation rates and the resulting volatile releases to air and worker inhalation exposures to that chemical vapor. The volatile air release models (discussed in C.2.1) calculate both a vapor generation rate ($Q_{vapor\_generation}$; g/sec) and the resulting daily release rate of the chemical vapors to air. The *EPA/OPPT Mass Balance Inhalation Model* (discussed in Section C.2.2) uses the value of $Q_{vapor\_generation}$, calculated by the appropriate release model, to estimate the resulting inhalation exposure to that released vapor.

B.2.1 Vapor Generation Rate and Volatile Air Release Models

The following models utilize a series of equations and default values to calculate a chemical vapor generation rate ($Q_{vapor\_generation}$; g/sec) and the resulting daily volatile air release rate ($Elocal_{air}$; kg/site-day):

- *EPA/OPPT Penetration Model* – evaporative releases from an exposed liquid surface located indoors;
- *EPA/OPPT Mass Transfer Coefficient Model* – evaporative releases from an exposed liquid surface located outdoors; and

- *EPA/OAQPS AP-42 Loading Model* – releases of volatile chemical contained in air that is displaced from a container being filled.

Each of these models is described in greater detail in the following sections:

B.2.1.1 EPA/OPPT Penetration Model

Model Description and Rationale:

The *EPA/OPPT Penetration Model* estimates releases to air from evaporation of a chemical from an open, exposed liquid surface. This model is appropriate for determining volatile releases from activities that are performed *indoors*[1] or when air velocities are expected to be *less than or equal to 100 feet per minute*.

A draft paper [Arnold and Engel, 1999] evaluating the relative performance of this model and the *Mass Transfer Coefficient Model* against experimentally measured evaporation rates described laminar airflow conditions existing up to 100 feet per minute. The paper compared the *Penetration Model* to experimental evaporation rate data measured under laminar (less than 100 feet per minute) and turbulent (above 100 feet per minute) airflow conditions. While the *Penetration Model* did not provide accurate estimates of evaporation rates under turbulent air flow conditions (relative to the *Mass Transfer Coefficient Model*), the results modeled under laminar flow conditions were found to more closely approximate the experimental data (usually within 20 percent). It is assumed that the conditions of an indoor work area most closely approximate laminar airflow conditions.

The model was originally developed using Fick's second law of diffusion. Model results were tested against experimental results of a study on evaporation rates for 15 compounds studied at different air velocities and temperatures in a test chamber. The experimental data confirmed the utility and accuracy of the model equation. Sample activities in which the *Penetration Model* may be used to estimate volatile releases to air are sampling liquids and cleaning liquid residuals from smaller transport containers (e.g., drums, bottles, pails).

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the exposed liquid surface using the following equation:

[B-1]

$$Q_{\mathrm{vapor\_generation}} = \frac{(8.24 \times 10^{-8}) \times \mathrm{MW}_{\mathrm{chem}}^{0.835} \times \mathrm{F}_{\mathrm{correction\_factor}} \times \mathrm{VP}_{\mathrm{chem}} \times \left(\frac{1}{29} + \frac{1}{\mathrm{MW}_{\mathrm{chem}}} \right)^{0.25} \times \mathrm{RATE}_{\mathrm{air\_speed}}^{0.5} \times \mathrm{AREA}_{\mathrm{opening}}}{\mathrm{TEMP}_{\mathrm{ambient}}^{0.05} \times \mathrm{D}_{\mathrm{opening}}^{0.5} \times \mathrm{P}_{\mathrm{ambient}}^{0.5}}$$

Where:

- $Q_{\mathrm{vapor\_generation}}$ = Average vapor generation rate (g of chemical/sec)

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[1] Similar air releases from surfaces located at *outdoor* locations (air speeds > 100 ft/min) are calculated using the *Mass Transfer Coefficient Model* (see the description provided in this section of Appendix B).

- $MW_{hem.}$ = Molecular weight of the chemical of interest (g/mol)
- $F_{correction\_factor}$ = Vapor pressure correction factor (EPA default =1)[1]
- $VP_{hem.}$ = Vapor pressure of the chemical of interest (torr)
- $RATE_{air\_speed}$ = Air speed (EPA default = 100 feet/min; value must be ≤ 100 feet/min for this model)
- $AREA_{opening}$ = Surface area of the static pool or opening (cm^2; $B \times D_{opening}^2 / 4$)
- $TEMP_{ambient}$ = Ambient temperature (EPA default = 298 K)
- $D_{opening}$ =Diameter of the static pool or opening (cm; See Table B-1 for appropriate EPA default values)
- $P_{ambient}$ =Ambient pressure (EPA default = 1 atm)

Note: The factor 8.24×10^{-8} in Equation B-1 accounts for various unit conversions. See Arnold and Engel, 1999, for the derivation of this constant.

Using the vapor generation rate ($Q_{vapor\_generation}$) calculated in Equation B-1, the model then estimates the daily release to air for the activity using the following equation:

$$Elocal_{air} = Q_{vapor\_generation} \times TIME_{activity\_hours} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \qquad [B\text{-}2]$$

Where:

- $Elocal_{air}$ = Daily release of the chemical vapor to air from the activity (kg/site-day)
- $Q_{vapor\_generation}$ = Average vapor generation rate (g of chemical/sec; see Equation B-1)
- $TIME_{activity\_hours}$ = Operating hours for the release activity per day (hours/site-day; See Table B-1 for appropriate EPA default values)

References:

Arnold, F.C. and Engel, A.J. Pre-publication draft article entitled, *Evaporation of Pure Liquids from Open Surfaces*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. October 1999.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-24 and Appendix K). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

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[1] The default vapor pressure correction factor, $F_{correction\_factor}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction\_factor} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material × VP_{chem}), thus the $F_{correction\_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

B.2.1.2 EPA/OPPT Mass Transfer Coefficient Model

Model Description and Rationale:

The *EPA/OPPT Mass Transfer Model* estimates releases to air from the evaporation of a chemical from an open, exposed liquid surface. This model is appropriate for determining this type of volatile release from activities that are performed *outdoors*[1] or when air velocities are expected to be *greater than 100 feet per minute*. A draft paper [Arnold and Engel, 1999] evaluating the relative performance of this and the *Penetration Model* against experimentally measured evaporation rates, described laminar airflow conditions existing up to 100 feet per minute. It is assumed that the conditions of an indoor process area most closely approximate laminar air flow conditions, while outdoor conditions approximate turbulent airflow conditions above 100 feet per minute.

As discussed in the draft paper, the model is predicated on the solution of the classical mass transfer coefficient model with the gas-phase mass transfer coefficient estimated by the correlation of Mackay and Matsugu. Results were tested against experimental results on 19 compounds generated by four different experimenters over a wide range of experimental conditions. While the *Mass Transfer Coefficient Model* matched the data well (usually within 20 percent), it was found that the *Penetration Model* (see description in previous section) outperformed the *Mass Transfer Coefficient Model* under laminar flow (i.e., "indoor") conditions. Therefore, the *Penetration Model* is used as a default for estimating indoor evaporation rates, while the *Mass Transfer Coefficient Model* is used for outdoor rates. Sample activities in which the *Mass Transfer Coefficient Model* may be used to estimate volatile releases to air are cleaning liquid residuals from process equipment and bulk transport containers (e.g., tank trucks, rail cars).

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the shallow pool using the following equation:

[B-3]

$$Q_{\text{vapor\_generation}} = \frac{(1.93 \times 10^{-7}) \times \text{MW}_{\text{chem}}^{0.78} \times \text{F}_{\text{correction\_factor}} \times \text{VP}_{\text{chem}} \times \left(\frac{1}{29} + \frac{1}{\text{MW}_{\text{chem}}} \right)^{0.33} \times \text{RATE}_{\text{air\_speed}}^{0.78} \times \text{AREA}_{\text{opening}}}{\text{TEMP}_{\text{ambient}}^{0.4} \times \text{D}_{\text{opening}}^{0.11} \times \left(\text{TEMP}_{\text{ambient}}^{0.5} - 5.87 \right)^{2/3}}$$

Where:

- $Q_{\text{vapor\_generation}}$ = Average vapor generation rate (g of chemical of interest/sec)
- MW_{chem} = Molecular weight of the chemical of interest (g/mol)
- $\text{F}_{\text{correction\_factor}}$ = Vapor pressure correction factor (EPA default =1)[2]

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[1] Similar air releases from surfaces located at *indoor* locations (air speeds ≤ 100 ft/min) are calculated using the *Penetration Model* (see the description provided in this section of Appendix B).

[2] The default vapor pressure correction factor, $\text{F}_{\text{correction\_factor}}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $\text{F}_{\text{correction\_factor}} \times \text{VP}_{\text{chem}}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material × VP_{chem}), thus the

- VP_{chem} =Vapor pressure of the chemical of interest (torr)
- $RATE_{air\_speed}$ = Air speed (EPA default = 440 feet/min; value must be > 100 feet/min for this model)
- $AREA_{opening}$ = Surface area of the static pool or opening (cm^2; $B \times D_{opening}^2 / 4$)
- $TEMP_{ambient}$ = Ambient temperature (EPA default = 298 K)
- $D_{opening}$ =Diameter of the static pool or opening (cm; See Table B-1 for appropriate EPA default values)

Note: The factor 1.93×10^{-7} in Equation B-3 accounts for various unit conversions. See Arnold and Engel, 1999, for the derivation of this constant.

Using the vapor generation rate ($Q_{vapor\_generation}$) calculated in Equation B-3, the model then estimates the daily release to air for the activity using the following equation:

$$Elocal_{air} = Q_{vapor\_generation} \times TIME_{activity\_hours} \times \frac{3600 \text{ sec/hour}}{1000 \text{ g/kg}} \qquad [B-4]$$

Where:

- $Elocal_{air}$ = Daily release of the chemical vapor to air from the activity (kg/site-day)
- $Q_{vapor\_generation}$ = Average vapor generation rate (g of chemical/sec; see Equation B-3)
- $TIME_{activity\_hours}$ = Operating hours for the release activity per day (hours/site-day; See Table B-1 for appropriate EPA default values)

References:

Arnold, F.C. and Engel, A.J. Pre-publication draft article entitled, *Evaporation of Pure Liquids from Open Surfaces*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. October 1999.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.2.1.3 EPA/OAQPS AP-42 Loading Model

Model Description and Rationale:

The EPA's Office of Air Quality Planning and Standards (OAQPS) *AP-42 Loading Model* estimates releases to air from the displacement of air containing chemical vapor as a container/vessel is filled with a liquid. This model assumes that the rate of evaporation is negligible compared to the vapor loss from the displacement.

$F_{correction\_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

This model is used as the default for estimating volatile air releases during both loading activities and unloading activities. This model is used for unloading activities because it is assumed while one vessel is being unloaded another is assumed to be loaded. The *EPA/OAQPS AP-42 Loading Model* is used because it provides a more conservative estimate than either the *EPA/OPPT Penetration Model* or the *Mass Transfer Coefficient Model* for unloading activities.

Model Equations:

The model first calculates the average vapor generation rate of the chemical from the displacement during loading/filling operation using the following equation:

[B-5]

$$Q_{vapor\_generation} = \frac{F_{saturation\_factor} \times MW_{chem} \times \left(V_{cont\_empty} \times \frac{3785.4\,cm^3}{gal} \right) \times \left(\frac{RATE_{fill}}{3600\ sec/hour} \right) \times F_{correction\_factor} \times \left(\frac{VP_{chem}}{760\ torr/atm} \right)}{R \times TEMP_{ambient}}$$

Where:

- $Q_{vapor\_generation}$ = Average vapor generation rate (g of chemical/sec)
- $F_{saturation\_factor}$ = Saturation factor (See Table B-1 for appropriate EPA default values)
- MW_{chem} = Molecular weight of the chemical of interest (g/mol)
- V_{cont_empty} = Volume of the container (gallons; see Table B-1 for appropriate EPA default values)
- $RATE_{fill}$ = Fill rate (containers/hour; see Table B-1 for appropriate EPA default values)
- $F_{correction\_factor}$ = Vapor pressure correction factor (EPA default =1)[1]
- VP_{chem} =Vapor pressure of the chemical of interest (torr)
- R =Universal Gas Constant (82.05 atm-cm^3/mol-K)
- $TEMP_{ambient}$ = Ambient temperature (EPA default = 298 K)

Using the vapor generation rate ($Q_{vapor\_generation}$) calculated in Equation B-5, the model then estimates the daily release to air for the activity using the following equation:

$$Elocal_{air} = Q_{vapor\_generation} \times TIME_{activity\_hours} \times \frac{3600\ sec/hour}{1000\ g/kg} \qquad [B\text{-}6]$$

Where:

- $Elocal_{air}$ = Daily release of the chemical vapor to air from the activity (kg/site-day)

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[1] The default vapor pressure correction factor, $F_{correction\_factor}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction\_factor} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material × VP_{chem}), thus the $F_{correction\_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

- $Q_{vapor\_generation}$ = Average vapor generation rate (g of chemical/sec; see Equation B-5)
- $TIME_{activity\_hours}$ = Operating hours for the release activity per day (hours/site-day; see Table B-1 for appropriate EPA default values)

Reference:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-21). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

Table B-1. Standard EPA Default Values Used in Vapor Generation Rate/Volatile Air Release Models

Activity Type (Location)	$V_{cont\ empty}$ (gallons)	$D_{opening}$ (cm)	$RATE_{fill}$ (containers/hour)	$F_{saturation\ factor}$	$TIME_{activity\ hours}$ (hours/site-day)
Container-Related Activities (e.g., filling, unloading, cleaning, open surface/evaporative losses):					
Bottles (Indoors)	1 (Range: <5)	5.08 (<5,000 gals)	60	Typical: 0.5 Worst Case: 1	Number of containers handled per site-day_) $RATE_{fill}$
Small Containers (Indoors)	5 (Range: 5 to <20)				
Drums (Indoors)	55 (Range: 20 to <100)		20		
Totes (Indoors)	550 (Range: 100 to <1,000)				
Tank Trucks (Outdoors)	5,000 (Range: 1,000 to <10,000)	7.6 (≥5,000 gals)	2	1	
Rail Car (Outdoors)	20,000 (Range: 10,000 and up)		1		
Equipment Cleaning Activities:					
Multiple Vessels (Outdoors)	Not applicable	92	Not applicable	1	4
Single, Large Vessel (Outdoors)					1
Single, Small Vessel (Outdoors)					0.5

Activity Type (Location)	**$V_{cont\ empty}$ (gallons)**	**$D_{opening}$ (cm)**	**$RATE_{fill}$ (containers/hour)**	**$F_{saturation\ factor}$**	**$TIME_{activity\ hours}$ (hours/site-day)**
Sampling Activities:					
Sampling Liquids (Indoors)	Not applicable	Typical: 2.5[a] Worst Case: 10	Not applicable	1	1
Other Activities:					
Continuous Operation	If other scenario-specific activities are identified that use one of the vapor generation rate/air release models described in this section, the ESD will describe the model and provide appropriate default values for the model parameters.			1	24
Batch Operation					Lesser of: (Hours/batch × Batches/site-day) or 24

a - The "typical" diameter default value of 2.5 cm was adopted as a policy decision in 2002, which supersedes the previous default value of 7 cm shown in the 1991 U.S. EPA reference document.

B.2.2 Chemical Vapor Inhalation Model

The following sections describe the EPA standard model for estimating worker inhalation exposures to a chemical vapor, utilizing a vapor generation rate ($Q_{vapor\_generation}$).

B.2.2.1 EPA/OPPT Mass Balance Model

Model Description and Rationale:

The *EPA/OPPT Mass Balance Model* estimates a worker inhalation exposure to an estimated concentration of chemical vapors within the worker's breathing zone. The model estimates the amount of chemical inhaled by a worker during an activity in which the chemical has volatilized and the airborne concentration of the chemical vapor is estimated as a function of the source vapor generation rate ($Q_{vapor\_generation}$). This generation rate may be calculated using an appropriate standard EPA vapor generation model (see Equation B-1, Equation B-3, or Equation B-5) or may be an otherwise known value.

The *EPA/OPPT Mass Balance Model* also utilizes the volumetric ventilation rate within a given space and includes simplifying assumptions of steady state (i.e., a constant vapor generation rate and a constant ventilation rate) and an assumed mixing factor for non-ideal mixing of air. The default ventilation rates and mixing factors provide a typical and worst case estimate for each exposure. The airborne concentration of the chemical cannot exceed the level of saturation for the chemical.

An evaluation of the model was performed against collected monitoring data for various activities (see the 1996 AIHA article). This evaluation confirmed that the Mass Balance Model is able to conservatively predict worker inhalation exposures within one order of magnitude of actual monitoring data and is an appropriate model for screening-level estimates.

Model Equations:

The model first calculates the volumetric concentration of the chemical vapor in air using the following equation:

$$C_{chem\_volumetric} = \frac{(1.7 \times 10^5) \times TEMP_{ambient} \times Q_{vapor\_generation}}{MW_{chem} \times RATE_{ventilation} \times F_{mixing\_factor}} \qquad [B-7]$$

Where:

- $C_{chem\_volumetric}$ = Volumetric concentration of the chemical vapor in air (ppm)
- $Q_{vapor\_generation}$ = Average vapor generation rate (g of chemical/sec; see Equation B-1, Equation B-3, or Equation B-5, as appropriate)
- $TEMP_{ambient}$ = Ambient temperature (EPA default = 298 K)
- MW_{chem} = Molecular weight of the chemical of interest (g/mol)
- $RATE_{ventilation}$ = Ventilation rate (ft^3/min; see Table B-2 for appropriate EPA default values)

- F_{mixing_factor} = Mixing factor (dimensionless; see Table B-2 for appropriate EPA default values)

Note: The factor 1.7×10^5 in Equation B-7 accounts for various unit conversions. See Fehrenbacher and Hummel, 1996, for the derivation of this constant.

Note that the airborne concentration of the chemical vapor cannot exceed the saturation level of the chemical in air. Equation B-8 calculates the volumetric concentration at the saturation level based on Raoult's Law. Use the lesser value for the volumetric concentration of the chemical vapor ($C_{chem\_volumetric}$) calculated in either Equation B-7 or Equation B-8 in calculating the mass concentration of the chemical of interest in the air (see Equation B-9).

$$C_{chem\_volumetric} = F_{correction\_factor} \times VP_{chem} \times \frac{10^6 \text{ ppm}}{P_{ambient}} \qquad [B\text{-}8]$$

Where:

- $C_{chem\_volumetric}$ = Volumetric concentration of the chemical of interest in air (ppm)
- $F_{correction\_factor}$ = Vapor pressure correction factor (EPA default =1)[1]
- VP_{chem} =Vapor pressure of the chemical of interest (torr)
- $P_{ambient}$ =Ambient pressure (default = 760 torr)

Note: Raoult's law calculates the airborne concentration as a mole fraction. The factor 10^6 in Equation B-8 accounts for the unit conversion from mole fraction to ppm.

The volumetric concentration of the chemical of interest in air (calculated in either Equation B-7 or Equation B-8) is converted to a mass concentration by the following equation:

$$C_{chem\_mass} = \frac{C_{chem\_volumetric} \times MW_{chem}}{V_{molar}} \qquad [B\text{-}9]$$

Where:

- C_{chem_mass} = Mass concentration of the chemical vapor in air (mg/m^3)
- $C_{chem\_volumetric}$ = Volumetric concentration of the chemical vapor in air (ppm, see Equation B-7 or B-8, as appropriate)
- MW_{chem} = Molecular weight of the chemical of interest (g/mol)
- V_{molar} =Molar volume (default = 24.45 L/mol at 25ºC and 1 atm)

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[1] The default vapor pressure correction factor, $F_{correction\_factor}$, assumes that the chemical-containing material in the evaporating pool exhibits the vapor pressure of the chemical of interest, as a worst case (i.e., effective VP of the evaporating material = $F_{correction\_factor} \times VP_{chem}$). Alternatively, Raoult's Law may be assumed (i.e., effective VP = mole fraction of the chemical in the material × VP_{chem}), thus the $F_{correction\_factor}$ may be set equivalent to the chemical's mole fraction in the material, if known. Note: in the absence of more detailed data, the chemical's weight fraction within the material formulation may be used to approximate its mole fraction.

Assuming a constant breathing rate for each worker and an exposure duration for the activity, the inhalation exposure to the chemical vapor during that activity can be estimated using the following equation:

$$EXP_{inhalation} = C_{chem\_mass} \times RATE_{breathing} \times TIME_{exposure} \quad [B\text{-}10]$$

Where:

- $EXP_{inhalation}$ = Inhalation exposure to the chemical vapor per day (mg chemical/worker-day)
- C_{chem_mass} = Mass concentration of the chemical vapor in air (mg/m^3; see Equation B-9]
- $RATE_{breathing}$ = Typical worker breathing rate (EPA default = 1.25 m^3/hr)
- $TIME_{exposure}$ = Duration of exposure for the activity (hours/worker-day; see Table B-2 for appropriate EPA default values ($\leq$ 8 hours/worker-day))

References:

Fehrenbacher, M.C. and Hummel, A.A[1]. "Evaluation of the Mass Balance Model Used by the EPA for Estimating Inhalation Exposure to New Chemical Substances". *American Industrial Hygiene Association Journal*. June 1996. 57: 526-536.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equation 4-21). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

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[1] Note: This reference is currently not available for viewing in the ChemSTEER Help System.

Table B-2. Standard EPA Default Values Used in the *EPA/OPPT Mass Balance Inhalation* Model

Activity Type (Location)	$V_{cont\ empty}$ (gallons)	$RATE_{fill}$ (containers/hour)	$RATE_{air\ speed}$ (feet/min)	$RATE_{ventilation}$ [a]	$F_{mixing\ factor}$	$TIME_{exposure}$ (hours/day)
Container-Related Activities (e.g., filling, unloading, cleaning, open surface/evaporative losses):						
Bottles (Indoors)	1 Range: <5	60	100 (Indoors)	Typical: 3,000 Worst Case: 500 (Indoors)	Typical: 0.5 Worst Case: 0.1	Lesser of: (Number of containers handled per site-day)) $RATE_{fill}$ or 8
Small Containers (Indoors)	5 Range: 5 to <20					
Drums (Indoors)	55 Range: 20 to <100	20				
Totes (Indoors)	550 Range: 100 to <1,000					
Tank Trucks (Outdoors)	5,000 Range: 1,000 to <10,000	2	440 (Outdoors)	Average: 237,600 Worst Case: $26{,}400 \times (60 \times RATE_{air\_speed}\ )\ 5{,}280)^3$ (Outdoors)		
Rail Car (Outdoors)	20,000 Range: 10,000 and up	1				
Equipment Cleaning Activities:						
Multiple Vessels (Outdoors)	Not applicable		440 (Outdoors)	Average: 237,600 Worst Case: $26{,}400 \times (60 \times RATE_{air\_speed}\ )\ 5{,}280)^3$ (Outdoors)	Typical: 0.5 Worst Case: 0.1	4
Single, Large Vessel (Outdoors)						1
Single, Small Vessel (Outdoors)						0.5

Table B-2 (Continued)

Activity Type (Location)	**V_{cont_empty} (gallons)**	**$RATE_{fill}$ (containers/hour)**	**$RATE_{air\_speed}$ (feet/min)**	**$RATE_{ventilation}$ [a]**	**F_{mixing_factor}**	**$TIME_{exposure}$ (hours/day)**
Sampling Activities:						
Sampling Liquids (Indoors)	Not applicable		100 (Indoors)	Typical: 3,000 Worst Case: 500 (Indoors)	Typical: 0.5 Worst Case: 0.1	1
Other Activities:						
Continuous Operation	If other scenario-specific activities are identified that use one of the vapor generation rate models with the *Mass Balance Inhalation Model* described in this section, the ESD will describe the models and provide appropriate default values for the model parameters.				Typical: 0.5 Worst Case: 0.1	≤8
Batch Operation						

a - If the appropriate vapor generation rate model is the *EPA/OAQPS AP-42 Loading Model* (see Equation B-5) for an outdoor activity, the $RATE_{air\_speed}$ should be set to 440 feet/min, as a default in determining the worst case $RATE_{ventilation}$.

B.3 CONTAINER RESIDUE RELEASE MODELS (NON-AIR)

Model Description and Rationale:

EPA has developed a series of standard models for estimating the quantity of residual chemical remaining in emptied shipping containers that is released to non-air media (e.g., water, incineration, or landfill) when the container is either rinsed or disposed. All of the residue models assume a certain portion or fraction of the chemical remains in the emptied container to be later rinsed or discarded with the empty container.

The default parameters of model are defined based upon the particular size/type of container (e.g., small containers, drums, or large bulk), as well as the physical form of the chemical residue (e.g., liquid or solid). These defaults are based upon data collected during a 1988 EPA-sponsored study of residuals in containers from which materials have been poured or pumped.

Model Equation:

All of the models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$Elocal_{container\_residue\_disp} = F_{container\_residue} \times Q_{total\_daily\_container} \qquad [B\text{-}11]$$

Where:

- $Elocal_{container\_residue\_disp}$ = Daily release of the chemical residue to water, incineration, or landfill from the cleaning or disposal of empty shipping containers (kg/site-day)
- $F_{container\_residue}$ = Fraction of the amount of the total chemical in the shipping container remaining in the emptied container (dimensionless; see Table B-3 for appropriate EPA default values)
- $Q_{total\_daily\_container}$= Total (daily) quantity of the chemical contained in the shipping containers prior to emptying (kg of chemical/site-day; see Table B-4 for appropriate EPA default values)

Each model, however, utilizes unique default values within that equation based upon the relative size of the container and the physical form of the chemical residue. These default values are summarized in Table B-3 and Table B-4. The following models are the standard EPA models for estimating container residues:

- *EPA/OPPT Small Container Residual Model*;
- *EPA/OPPT Drum Residual Model*;
- *EPA/OPPT Bulk Transport Residual Model*; and
- *EPA/OPPT Solid Residuals in Transport Containers Model.*

The default frequency with which the container residues are released ($TIME_{days\_container\_residue}$, days/site-year) must be appropriately “paired” with the total daily quantity of chemical contained in the containers ($Q_{total\_daily\_container}$) used in calculating the daily release. Thus, Table B-4 also contains the appropriate EPA default values for $TIME_{days\_container\_residue}$.

References:

U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.

U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment.* July 1988.

Table B-3. Standard EPA Default Values for Use in the Container Residual Release Models

Chemical Form	Container Type	V_{cont_empty} (gallons)	Model Title	$F_{container\_residue}$[a]
Liquid	Bottle	1 Range: <5	*EPA/OPPT Small Container Residual Model*	Central Tendency: 0.003 High End: 0.006
	Small Container	5 Range: 5 to <20		
	Drum	55 Range: 20 to <100	*EPA/OPPT Drum Residual Model*	Central Tendency: 0.025 High End[b]: 0.03 (for pumping liquid out of the drum) Alternative defaults: Central Tendency: 0.003 High End: 0.006 (for pouring liquid out of the drum)
	Tote	550 Range: 100 to <1,000	*EPA/OPPT Bulk Transport Residual Model*	Central Tendency: 0.0007 High End: 0.002
	Tank Truck	5,000 Range: 1,000 to <10,000		
	Rail Car	20,000 Range: 10,000 and up		
Solid	Any	Any	*EPA/OPPT Solid Residuals in Transport Containers Model*	0.01

a – These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see *References* in this section for the citations of these sources).

B – The 1992 EPA memorandum reference document contains the previous default of 0.04 for the high-end loss fraction ($F_{container\_residue}$) for the *Drum Residual Model*; however, this value was superseded by an internal policy decision in 2002. Per 40 CFR 261.7(b)(1) of the Resource Conservation and Recovery Act (RCRA), "a container or an inner liner removed from a container that has held any hazardous wastes, except waste that is a compressed gas or that is identified as an acute hazardous waste…is empty if…(ii) no more than 2.5 centimeters (1 inch) remain on the bottom of the container or liner or (iii)(A) no more than 3 percent by weight of the total capacity of the container remains in the container or inner liner if the container is equal to or less than 110 gallons in size…". The 3 percent high-end default is consistent with the range of experimental results documented in the 1988 EPA study (see *References* in this section for a citation of this study).

Table B-4. Standard EPA Methodology for Calculating Default $Q_{total\_daily\_container}$ and $TIME_{days\_container\_residue}$ Values for Use in the Container Residual Models

Number of Containers Emptied per Day	Qtotal_daily_container (kg/site-day)	TIMEdays_container_residue (days/year)
1 or more	(Mass quantity of chemical in each container (kg/container)) × (Number of containers emptied per day)	Total number of operating days for the facility/operation
Less than 1	Mass quantity of chemical in each container (kg/container)	Total number of containers emptied per site-year

B.4 PROCESS EQUIPMENT RESIDUE RELEASE MODELS (NON-AIR)

Model Description and Rationale:

EPA has developed two standard models for estimating the quantity of residual chemical remaining in emptied process equipment that is released to non-air media (e.g., water, incineration, or landfill) when the equipment is periodically cleaned and rinsed. The residue models assume a certain portion or fraction of the chemical remains in the emptied vessels, transfer lines, and/or other equipment and is later rinsed from the equipment during cleaning operations and discharged with the waste cleaning materials to an environmental medium.

The default parameters of the model are defined based upon whether the residues are being cleaned from a *single* vessel or from *multiple* pieces of equipment. These defaults are based upon data collected during an EPA-sponsored study of residuals in process equipment from which materials have pumped or gravity-drained.

Model Equation:

The models discussed in this section utilize the following common equation for calculating the amount of chemical residue:

$$\text{Elocal}_{\text{equip\_cleaning}} = \text{F}_{\text{equip\_residue}} \times \text{Q}_{\text{total\_chem\_capacity}} \qquad \text{[B-12]}$$

Where:

- $\text{Elocal}_{\text{equip\_cleaning}}$ = Daily release of the chemical residue to water, incineration, or landfill from cleaning of empty process equipment (kg/site-day)
- $\text{F}_{\text{equip\_residue}}$ = Fraction of the amount of the total chemical in the process equipment remaining in the emptied vessels, transfer lines, and/or other pieces (dimensionless; see Table B-5 for appropriate EPA default values)
- $\text{Q}_{\text{equip\_chem\_capacity}}$ = Total capacity of the process equipment to contain the chemical in question, prior to emptying (kg of chemical/site-day; see Table B-6 for appropriate EPA default values)

Each model, however, utilizes unique default values within that equation based upon whether the residues are cleaned from a single vessel or from multiple equipment pieces. These default values are summarized in Table B-5 and Table B-6. The following models are the standard EPA models for estimating process equipment residues:

- *EPA/OPPT Single Process Vessel Residual Model; and*
- *EPA/OPPT Multiple Process Vessel Residual Model.*

The default frequency with which the equipment residues are released ($\text{TIME}_{\text{days\_equip\_residue}}$, days/site-year) must be appropriately “paired” with the total capacity of the equipment to contain the chemical of interest ($\text{Q}_{\text{equip\_chem\_capacity}}$) used in calculating the daily release. Thus, Table B-6 also contains the appropriate EPA default values for $\text{TIME}_{\text{days\_equip\_residue}}$.

References:

U.S. EPA. Chemical Engineering Branch. Memorandum: *Standard Assumptions for PMN Assessments*. From the CEB Quality Panel to CEB Staff and Management. October 1992.

U.S. EPA. Office of Pesticides and Toxic Substances. *Releases During Cleaning of Equipment.* July 1988.

Table B-5. Standard EPA Default Values for Use in the Process Equipment Residual Release Models

Model Title	$F_{equip\ residue}$[a]
EPA/OPPT Single Process Vessel Residual Model	Conservative: 0.01 (for pumping process materials from the vessel) *Alternative defaults: Central Tendency: 0.0007 High End to Bounding: 0.002 (alternative defaults for gravity-draining materials from the vessel)
EPA/OPPT Multiple Process Vessel Residual Model	Conservative: 0.02

a - These defaults are based on the 1988 EPA study investigating container residue and summarized in the 1992 internal EPA memorandum (see References in this section for the citations of these sources).

Table B-6. Standard EPA Methodology for Calculating Default $Q_{equip\_chem\_capacity}$ and $TIME_{days\_equip\_residue}$ Values for Use in the Process Equipment Residual Models

Process Type	Number of Batches per Day	$Q_{equip\ chem.\ capacity}$ (kg/site-day)	$TIME_{days\ equip\ residue}$ (days/year)
Batch	1 or more	(Mass quantity of chemical in each batch (kg/batch)) × (Number of batches run per day)	Total number of operating days for the facility/operation
	Less than 1	Mass quantity of chemical in each batch (kg/batch)	Total number of batches run per site-year
Continuous	Not applicable	Daily quantity of the chemical processed in the equipment (kg/site-day)	Total number of operating days for the facility/operation

Note: Please refer to the ESD for any overriding default assumptions to those summarized above. Equipment cleaning may be performed periodically throughout the year, as opposed to the default daily or batch-wise cleaning frequencies shown above. For example, facilities may run dedicated equipment for several weeks, months, etc within a single campaign before performing equipment-cleaning activities, such that residuals remaining in the emptied are released less frequently than the standard default $TIME_{days\_equip\_residue}$ summarized above in Table B-6. Care should be given in defining the appropriate $Q_{total\_daily\_container}$ and $TIME_{days\_container\_residue}$ to be used in either of the standard EPA process equipment residue models.

B.5 CHEMICAL PARTICLE INHALATION EXPOSURE MODELS

The following EPA standard models may be used to estimate worker inhalation exposures to particles containing the chemical of interest:

- *EPA/OPPT Small Volume Solids Handling Inhalation Model*; and
- *OSHA Total Particulates Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL)-Limiting Model.*

Each of these models is an alternative default for calculating worker inhalation exposures during the following particulate-handling activities, based upon the relative daily amount of particulate material being handled:

- Unloading and cleaning solid residuals from transport containers/vessels;
- Loading solids into transport containers/vessels; and
- Cleaning solid residuals from process equipment.

For amounts up to (and including) 54 kg/worker-shift, the *EPA/OPPT Small Volume Solids Handling Inhalation Model* is used, as it more accurately predicts worker exposures to particulates within this range than the *OSHA Total PNOR PEL-Limiting Model*. The *Small Volume Solids Handing Inhalation Model* is based on exposure monitoring data obtained for workers handling up to 54 kg of powdered material. Beyond this data-supported limit, EPA assumes that exposures within occupational work areas are maintained below the regulation-based exposure limit for “particulates, not otherwise regulated”.

The *EPA/OPPT Small Volume Solids Handling Model* is also the exclusive model used for any solids sampling activity. Each of these models is described in detail in the following sections.

B.5.1 EPA/OPPT Small Volume Solids Handling Inhalation Model

Model Description and Rationale:

The *EPA/OPPT Small Volume Solids Handling Inhalation Model* utilizes worst case and typical exposure factors to estimate the amount of chemical inhaled by a worker during handling of *small volumes*[1] (i.e., $\leq$54 kg/worker-shift) of solid/powdered materials containing the chemical of interest. The handling of these small volumes is presumed to include scooping, weighing, and pouring of the solid materials.

The worst case and typical exposure factor data were derived from a study of dye weighing and adapted for use in situations where workers are presumed to handle small volumes of solids in a manner similar to the handling in the study. The maximum amount of dye handled in the study was 54 kg/worker-shift, so the *Small Volume Solids Handling Inhalation Model* is presumed to be valid for quantities up to and including this amount. In the absence of more specific exposure data for the particular activity, EPA uses these data to

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[1] Worker inhalation exposures to particulates handled in amounts *greater than 54 kg/worker-shift* are calculated using the *OSHA Total PNOR PEL-Limiting Model* (see the description provided in this section of Appendix B).

estimate inhalation exposures to solids transferred at a rate up to and including 54 kg/worker-shift. This model assumes that the exposure concentration is the same as the concentration of the chemical of interest in the airborne particulate mixture.

Note that the amount handled per worker per shift is typically unknown, because while the throughput may be known, the number of workers and the breakdown of their activities are typically unknown. For example, while two workers may together handle 100 kg of material/day, one worker may handle 90 kg of material/day and the other may only handle 10 kg of material/day. Therefore, as a conservative estimate EPA assumes that the total throughput ($Q_{facility\_day}$; kg/site-day) is equal to the amount handled per worker ($Q_{shift\_handled}$; kg/worker-shift), if site-specific information is not available.

Model Equation:

The model calculates the inhalation exposure to the airborne particulate chemical using the following equation:

$$EXP_{inhalation} = (Q_{shift\_handled} \times N_{shifts}) \times F_{chem} \times F_{exposure} \quad [B-13]$$

Where:

- $EXP_{inhalation}$ = Inhalation exposure to the particulate chemical per day (mg chemical/worker-day)
- $Q_{shift\_handled}$ = Quantity of the solid/particulate material containing the chemical of interest that is handled by workers each shift (kg/worker-shift; see Table B-7 for appropriate EPA default values; must be ≤54 kg/worker-shift for this model to be valid)
- N_{shifts}[1] =Number of shifts worked by each worker per day (EPA default = 1 shift/day)
- F_{chem} =Weight fraction of the chemical of interest in the particulate material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value)
- $F_{exposure}$=Exposure factor; amount of total particulate handled that is expected to be inhaled (EPA defaults: 0.0477 mg/kg (typical) and 0.161 mg/kg (worst case))

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[1] Note that this value is the number of shifts worked by *each worker* per day. This value would only be greater than one if a worker worked for over eight hours in a given day.

Table B-7. Standard EPA Default Values for $Q_{daily\_handled}$ in the *EPA/OPPT Small Volume Solids Handling Inhalation Model*

Activity Type	Default $Q_{shift\ handled}$ [1] (kg/worker-day)
Loading and Unloading Containers	Quantity of material in each container (kg/container) × Number of containers/worker-shift
Container Cleaning	Quantity of residue in each container (kg/container) × Number of container/worker-shift
Process-Related Activity (equipment cleaning, sampling):	
Continuous process:	Daily throughput of material / Number of shifts per day
Batch process (<1 batch per day):	Quantity of material per batch
Batch process (>1 batch per day):	Quantity of material per batch × Number of batches per shift

References:

U.S. EPA. Chemical Engineering Branch. Generic Scenario: *Textile Dyeing*. October 15, 1992.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (page 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

U.S. EPA Economics, Exposure and Technology Division[2]. *Textile Dye Weighing Monitoring Study*. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington D.C., EPA 560/5-90-009. April 1990.

B.5.2 OSHA Total PNOR PEL-Limiting Model

Model Description and Rationale:

The *OSHA Total Particulates Not Otherwise Regulated (PNOR) Permissible Exposure Limit (PEL)-Limiting Model* estimates the amount of chemical inhaled by a worker during handling of solid/powdered materials containing the chemical of interest. The estimate assumes that the worker is exposed at a level no greater than the OSHA PEL for *Particulate, Not Otherwise Regulated*, total particulate. Operations are generally expected to comply with OSHA's federal regulation regarding total particulate exposures. This model assumes that the exposure concentration is the same as the concentration of the chemical of interest in the airborne particulate mixture.

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[1] The appropriate quantity of material handled by each worker on each day may vary from these standard CEB defaults, per the particular scenario. Be sure to consult the discussion presented in the ESD activity description in determining the most appropriate default value for $Q_{daily\_handled}$.

[2] Note: This reference is currently available for viewing in the ChemSTEER Help System.

The *OSHA Total PNOR PEL-Limiting Model* is used in cases where workers are handling quantities of solid/powdered materials *in excess of 54 kg/worker-shift*[1]. As stated in Section C.5, the *Small Volume Solids Handling Model*, based on monitoring data, provides a more realistic estimate of worker inhalation exposures to smaller quantities particulate material. The data used by the *Small Volume Solids Handling Model* are supported up to and including 54 kg solid material handled per worker-shift. Beyond this amount, EPA assumes the occupational exposures are maintained below the regulatory exposure limit contained in the *OSHA Total PNOR PEL-Limiting Model*, although the exposures provided by this model are considered to be worst-case, upper-bounding estimates.

Refer to Table B-7 for the standard EPA assumptions used in determining the appropriate quantity of particulate material handled to determine the applicability of this model to a given activity.

NOTE: The OSHA Total PNOR PEL (used as the basis for the model calculations) is an 8-hour time-weighted average (TWA); therefore, *worker exposures must be assumed to occur over an 8-hour period* for the *OSHA Total PNOR PEL-Limiting Model* estimate to be valid basis for the calculated inhalation exposure estimate.

Model Equations:

The model first calculates the mass concentration of the airborne particulate chemical using the following equation:

$$C_{chem\_mass} = C_{total\_mass} \times F_{chem} \qquad [B\text{-}14]$$

Where:

- C_{chem_mass} = Mass concentration of the chemical in air (mg/m^3)
- C_{total_mass}= Mass concentration of total particulate (containing the chemical) in air (EPA default = 15 mg/m^3, based on the OSHA Total PNOR PEL, 8-hr TWA)
- F_{chem} =Weight fraction of the chemical of interest in the particulate material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value)

Similar to Equation B-10 in the *EPA/OPPT Mass Balance Inhalation Model*, the *OSHA Total PNOR PEL-Limiting Model* then uses the mass airborne concentration of the chemical (C_{mass_chem}) in Equation B-14, to calculate the inhalation exposure to the particulate chemical using the following equation:

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[1] Worker inhalation exposures to particulates handled in amounts *up to and including 54 kg/worker-shift* are calculated using the *EPA/OPPT Small Volume Handling Inhalation Model* (see the description provided in this section of Appendix B).

$$EXP_{inhalation} = C_{chem\_mass} \times RATE_{breathing} \times TIME_{exposure} \qquad [B-15]$$

Where:

- $EXP_{inhalation}$ = Inhalation exposure to the airborne particulate chemical per day (mg chemical/worker-day)
- C_{chem_mass} = Mass concentration of the particulate chemical in air (mg/m^3; see Equation B-14)
- $RATE_{breathing}$ = Typical worker breathing rate (EPA default = 1.25 m^3/hr)
- $TIME_{exposure}$ = Duration of exposure for the activity (EPA default = 8 hours/worker-day[1])

References:

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1 (Equations 4-1 and 4-11). U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

B.6 DERMAL EXPOSURE MODELS

Model Description and Rationale:

EPA has developed a series of standard models for estimating worker dermal exposures to liquid and solid chemicals during various types of activities. All of these dermal exposure models assume a specific surface area of the skin that is contacted by a material containing the chemical of interest, as well as a specific surface density of that material in estimating the dermal exposure. The models also assume *no use of controls or gloves* to reduce the exposure. These assumptions and default parameters are defined based on the nature of the exposure (e.g., one hand or two hand, immersion in material, contact with surfaces) and are documented in the references listed in this section.

In the absence of data, the EPA/OPPT standard models for estimating dermal exposures from industrial activities described in this section can be used. The models for exposures to liquid materials are based on experimental data with liquids of varying viscosity and the amount of exposure to hands was measured for various types of contact. Similar assessments were made based on experimental data from exposure to solids.

Model Equation:

All of the standard EPA models utilize the following common equation for calculating worker dermal exposures:

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[1] Since the OSHA Total PNOR PEL is an 8-hr TWA, the exposure duration must be assumed as 8 hours/worker-day for the model defaults to apply.

$$EXP_{dermal} = AREA_{surface} \times Q_{remain\_skin} \times F_{chem} \times N_{event} \quad [B-16]$$

Where:

- EXP_{dermal} = Dermal exposure to the liquid or solid chemical per day (mg chemical/worker-day)
- $AREA_{surface}$ = Surface area of the skin that is in contact with liquid or solid material containing the chemical (cm^2; see Table B-8 for appropriate EPA default values)
- Q_{remain_skin} = Quantity of the liquid or solid material containing the chemical that remains on the skin after contact (mg/cm^2-event; see Table B-8 for appropriate EPA default values)
- F_{chem} =Weight fraction of the chemical of interest in the material being handled in the activity (dimensionless; refer to the ESD discussion for guidance on appropriate default value)
- N_{event}[1] =Frequency of events for the activity (EPA default = 1 event/worker-day)

Each model, however, utilizes unique default values within that equation based upon the nature of the contact and the physical form of the chemical material. These default values are summarized in Table B-8. The following models are the standard EPA models for estimating worker dermal exposures:

- *EPA/OPPT 1-Hand Dermal Contact with Liquid Model*;
- *EPA/OPPT 2-Hand Dermal Contact with Liquid Model*;
- *EPA/OPPT 2-Hand Dermal Immersion in Liquid Model*;
- *EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model;* and
- *EPA/OPPT 2-Hand Dermal Contact with Solids Model.*

For several categories of exposure, EPA uses qualitative assessments to estimate dermal exposure. Table B-9 summarizes these categories and the resulting qualitative dermal exposure assessments.

References:

U.S. EPA. Chemical Engineering Branch. *Options for Revising CEB's Method for Screening-Level Estimates of Dermal Exposure – Final Report.* U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. June 2000.

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[1] Only one contact per day (N_{event} = 1 event/worker-day) is assumed because Q_{remain_skin}, with few exceptions, is not expected to be significantly affected either by wiping excess chemical material from skin or by repeated contacts with additional chemical material (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical material adhering to the skin and additional contacts with the chemical material do not add a significant fraction to the layer). Exceptions to this assumption may be considered for chemicals with high volatility and/or with very high rates of absorption into the skin.

U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

Table B-8. Standard EPA Default Values for Use in the Worker Dermal Exposure Models

Default Model	**Example Activities**	**$AREA_{surface}$[a] (cm^2)**	**$Q_{remain\ skin}$[b] (mg/cm^2-event)**	**Resulting Contact $AREA_{surface} \times Q_{remain\ skin}$ (mg/event)**
Physical Form: Liquids				
EPA/OPPT 1-Hand Dermal Contact with Liquid Model	• Liquid sampling activities • Ladling liquid/bench-scale liquid transfer	420 (1 hand mean)	Low: 0.7 High: 2.1	Low: 290 High: 880
EPA/OPPT 2-Hand Dermal Contact with Liquid Model	• Maintenance • Manual cleaning of equipment and containers • Filling drum with liquid • Connecting transfer line	840 (2 hand mean)	Low: 0.7 High: 2.1	Low: 590 High: 1,800
EPA/OPPT 2-Hand Dermal Immersion in Liquid Model	• Handling wet surfaces • Spray painting	840 (2 hand mean)	Low: 1.3 High: 10.3	Low: 1,100 High: 8,650
Physical Form: Solids				
EPA/OPPT 2-Hand Dermal Contact with Container Surfaces Model	• Handling bags of solid materials (closed or empty)	No defaults	No defaults	< 1,100[c]
EPA/OPPT 2-Hand Dermal Contact with Solids Model	• Solid sampling activities • Filling/dumping containers of powders, flakes, granules • Weighing powder/scooping/mixing (i.e., dye weighing) • Cleaning solid residues from process equipment • Handling wet or dried material in a filtration and drying process	No defaults	No defaults	< 3,100[23]

a - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citations of this sources) and are the mean values for men taken from the EPA Exposure Factors Handbook, 1997.

b - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source). The report derived the selected ranges of values for liquid handling activities from: U.S. EPA. A Laboratory Method to Determine the Retention of Liquids on the Surface of Hands. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Exposure Evaluation Division. EPA 747-R-92-003. September 1992.

c - These default values were adopted in the 2000 EPA report on screening-level dermal exposure estimates (see *References* in this section for the citation of this source). The report derived values for dermal contact for solids handling activities from: Lansink, C.J.M., M.S.C. Breelen, J. Marquart, and J.J. van Hemmen: Skin Exposure to Calcium Carbonate in the Paint Industry. Preliminary Modeling of Skin Exposure Levels to Powders Based on Field Data (TNO Report V 96.064). Rijswijk, The Netherlands: TNO Nutrition and Food Research Institute, 1996

Table B-9. EPA Default Qualitative Assessments for Screening-Level Estimates of Dermal Exposure

Category	Dermal Assessment
Corrosive substances (pH>12, pH<2)	Negligible
Materials at temperatures >140°F (60°C)	Negligible
Cast Solids (e.g., molded plastic parts, extruded pellets	Non-Quantifiable (Some surface contact may occur if manually transferred)
"Dry" surface coatings (e.g., fiber spin finishes, dried paint)	Non-Quantifiable (If manual handling is necessary and there is an indication that the material may abrade from the surface, quantify contact with fingers/palms as appropriate)
Gases/Vapors	Non-Quantifiable (Some contact may occur in the absence of protective clothing)

Source: U.S. EPA. Chemical Engineering Branch. *CEB Manual for the Preparation of Engineering Assessment*, Volume 1. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC. Contract No. 68-D8-0112. February 1991.

APPENDIX C:

ADDITIONAL REFERENCES

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APPENDIX D:

OTHER SEMICONDUCTOR MANUFACTURING STEPS WITH NO PHOTORESIST RELEASES

Descriptions of the semiconductor manufacturing steps other than photolithography and etching are provided below. These steps are documented to establish that no photoresist releases are expected beyond the photolithography and etching steps.

Oxidation

The first step in wafer fabrication is oxidation. The oxidation process forms a layer of silicon dioxide on the surface via a chemical reaction to protect the wafer from later processing steps. The wafer is heated in an oxygen-filled chamber to over 1500°F. Chemical vapor deposition (CVD) is used to bind a layer of silicon dioxide onto the surface of the wafer.

The materials used in oxidation include oxygen and silicon dioxide. Acids (e.g., hydrofluoric) and solvents are used to clean and dry the wafer following the oxidation process. The main sources of release from this process are organic solvent vapors, rinsewaters, and spent acids and solvents from cleaning the wafers.

Doping

Doping is a process in which specific atoms of impurities are introduced into the silicon substrate to alter the electrical properties of the substrate by acting as charge carriers. Their concentration and type dictate the electrical characteristics that define the function of the semiconductor. Doping is typically accomplished through ion implantation or diffusion processes.

Ion implantation is the most common method used to introduce impurity atoms into the wafer. It provides a more controlled doping mechanism than diffusion. The dopant atoms are first ionized with a medium-to-high-current filament, then accelerated toward the wafer surface with large magnetic and electrical fields. Strictly governing the dopant ion momentum allows for precise control of the penetration into the silicon substrate. The high kinetic energy of the ions during bombardment damages the substrate=s crystalline structure. To restore the substrate=s structure to a satisfactory level, the amorphous material is slowly heated or Aannealed@ in various gaseous atmospheres.

Diffusion is a high-temperature process also used to introduce a controlled amount of a dopant into the silicon substrate. Dopants are introduced in a specially designed tube furnace through either gaseous or nongaseous diffusion. In gaseous diffusion, dopant gases are introduced into the furnace to diffuse into the exposed areas of the substrate. Alternatively, in nongaseous diffusion, the furnace heat allows dopant atoms from a previously deposited dopant oxide layer to diffuse into the substrate in the areas where the two are in contact. By knowing the amount of dopant atoms and using a carefully controlled constant temperature, a predictable solid-state diffusion may be achieved.

Table D-1 lists examples of typical chemicals used and waste generated in the doping process and Figure D-1 shows a process flow diagram of the processes.

The most common potential sources of chemical releases from doping are the dopants themselves, as well as certain organic compounds that may be used as furnace cleaning gases or chlorine sources. Potential release sources include tool and control device exhaust vents, spent cleaning solutions, and solid or hazardous waste generated as part of the process. Organic chemicals may be emitted from furnace exhaust and may also be collected and sent off site for further waste management. Although low quantities of dopant metals are used, they may be found in trace amounts in wastewater treatment plant effluent or solid waste shipped off site for further waste management.

Table D-1. Materials Used and Waste Generated During the Doping Process

Dopants	Waste Generated
Common Compounds Antimony Arsenic Phosphorus Boron **Other Dopants Used** Aluminum Arsine Boron Triflouride Diborane Gallium Gold Beryllium Germanium Magnesium Silicon Tin Tellurium	**Wastewater Contaminants (to POTW or off-site transfer)** Antimony Arsenic Phosphorus Boron (plus other dopants used) **Air Contaminants** Excess dopant gases Contaminated carrier gases Out-gassed dopant gases

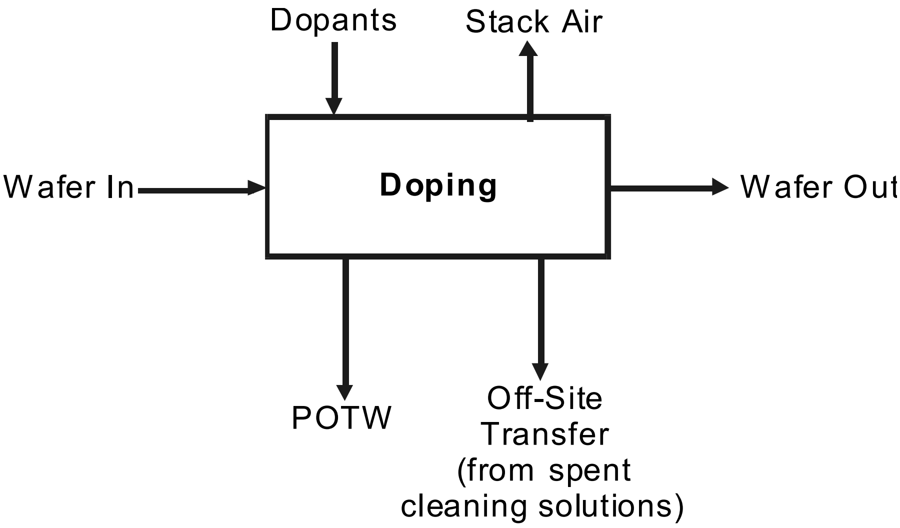

Figure D-1. Process Flow Diagram for Typical Doping Process

Thin Film Deposition

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

- Single crystal silicon films (also called epitaxial silicon): Substrate in which the hearts of transistors are constructed.
- Amorphous silicon films (also called polysilicon): Gate electrodes in most modern devices. Typically heavily doped to make them very conductive.
- Silicon nitride films: Passivation layers that are used primarily as protective layers after most device processing has occurred; may also be used as an etch stop in some cases.
- Silicon dioxide films: Dielectric layers; may also act as masks for subsequent processing. Deposited by using silicon and oxygen precursor compounds or are oxidized using wet or dry oxidation processes. Are most frequently deposited films.

Deposition of these films is frequently performed in a CVD reactor or a high-temperature tube furnace using silicon-containing gases as reactants. The deposition rate can be further enhanced by striking plasma to overcome kinetic barriers. Selected impurity compounds or dopants may be used in the deposition process to alter the electrical characteristics of the deposited film or layer. Sometimes a chlorine source is used during oxidation to modify the oxide characteristics.

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

Table D-2 lists typical chemicals used in the thin film deposition process, and Figure D-2 shows a typical process flow diagram for the process.

Thin film furnace or oxidation chamber exhaust (from venting gas left unreacted after CVD process or from purging the reactor and transport lines after the process is completed [CEB, 1994b][29]) is typically routed to a scrubber that vents to the atmosphere, and also results in wastewater generation. The exhaust may also be routed to an incinerator [CEB, 1994b]. Release sources from the application of thin films include ammonia gas used as a nitrogen source in silicon nitride deposition, organics used as chlorine sources, organics used to clean deposition furnaces, and metals deposited to interconnect electrical devices. This operation is performed in a robotically controlled cleanroom environment with no human intervention.

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[29] [CEB, 1994b] *Generic Scenario: Film Deposition in Integrated Circuit Fabrication*; U.S. EPA; Office of Pollution Prevention and Toxics; Chemical Engineering Branch; Washington, DC; 1994.

Table D-2. Materials Used and Waste Generated During Thin Film Deposition

Materials Used	Waste Generated
Ammonia Anhydrous ammonia (gas) Arsenic Arsine Boron Chlorine Crystal silicon (aka Epitaxial silicon) Diborane 1,2-dichloroethylene Hydrogen Nitrogen Nitrous oxide Phosphine Polysilicon (aka amorphous silicon) Silane Silicon nitride Silicon tetrachloride Trifluoride Tungsten hexafluoride	Acid fumes from etching operations Organic solvent vapors from cleaning resist drying, from developing, and from etching (resist stripping hydrogen chloride vapors) Rinsewaters containing acids and organic solvents (from cleaning, developing, etching, and resist stripping processes) Rinsewaters from aqueous developing systems Spent etchant solutions Spent solvents (including F003) Spent acid baths

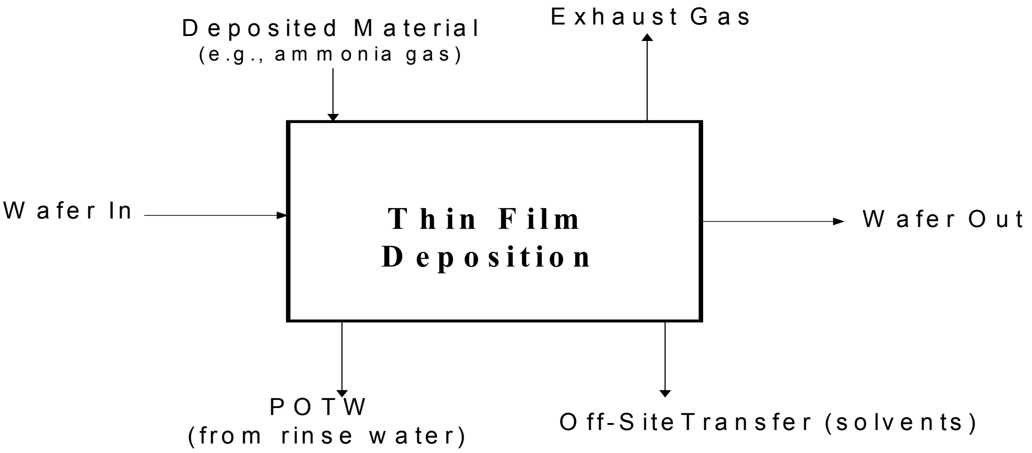

Figure D-2. Process Flow Diagram for the Thin Film Deposition Process

Chemical Mechanical Planarization

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

Figure D-3 presents a process flow diagram of the CMP processes. Spent slurry containing nitrates from the planarization process is typically transferred off site to a POTW.

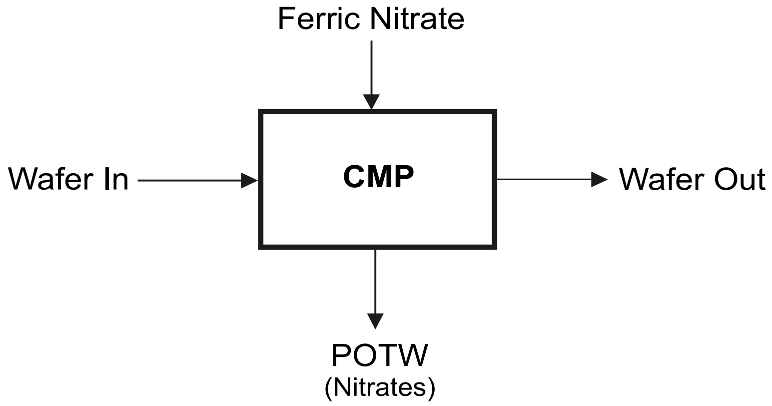

Figure D-3. Process Flow Diagram for Typical Chemical Mechanical Planarization Process

Metallization

Metallization is the process by which conductive metal is deposited onto the wafer to form the conductive layers of the chip. While aluminum has been the metal of choice, modern devices are now using copper as the conductor. Deposition is accomplished through a variety of techniques including evaporation, electrodeposition, electroplating, atomic layering, and chemical vapor deposition.

Cleaning

Wafer cleaning is required to ensure that contaminants on the wafer surfaces do not affect the final integrated circuit=s electrical performance. Before (and sometimes after) wafers are subjected to any specialized manufacturing processes, they are typically immersed in or sprayed with various aqueous and/or organic solutions. In some cases, they are mechanically scrubbed to remove films, residues, bacteria, or other particles. Fog chambers may also be used for wafer cleaning. The process equipment is also cleaned using inorganic acids and organic solvents.

Table D-3 lists examples of typical chemicals used and waste generated in the cleaning process, and Figure D-4 presents a process flow diagram of the process. Waste solvents used in cleaning operations may be either directly discharged to surface water after on-site treatment or transferred off site to a POTW. Stack and fugitive air emissions, which may include acid fumes and organic solvent vapors, may be released from cleaning station exhaust vents.

Table D-3. Cleaning Materials Used and Waste Generated During the Cleaning Process

Cleaning Materials Used	Waste Generated
Deionized water Isopropyl alcohol Acetone Methanol Hydroxylamine* NMP*	Spent solvents and acids in the wastewater and rinsewater Acid fumes and organic solvent vapors Container residue Spent solvents

a - Added to this version per SIA suggestion.

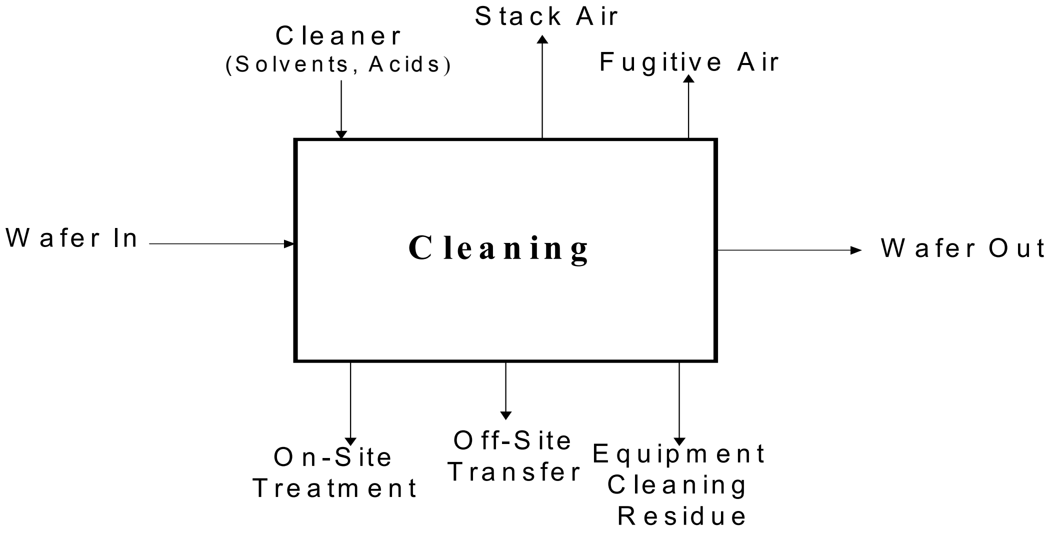

Figure D-4. Process Flow Diagram for Typical Cleaning Process