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EMISSION SCENARIO DOCUMENT ON PHOTORESIST USE IN SEMICONDUCTOR MANUFACTURING

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EMISSION SCENARIO DOCUMENT ON PHOTORESIST USE IN SEMICONDUCTOR MANUFACTURING

Environment Directorate

Organisation for Economic Co-operation and Development

June 2004

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The Environmental Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organization Programme for the Sound Management of Chemicals (IOMC) was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and the OECD (the Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. UNITAR joined the IOMC in 1997 to become the seventh Participating Organization. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals present in photoresist materials used in semiconductor manufacturing to assist in the estimation of releases of chemicals to the environment. Photoresists are polymer-based liquids applied in layers to create patterns on the silicon wafers.

This ESD should be seen as a 'living' document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other that 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). 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

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

Coverage

This ESD presents a standardised approach to estimate potential occupational exposures and environmental releases from non-volatile chemicals present within photoresist materials used in manufacture of semi-conductors (Industry Category 4 – electrical/electronic industry). These approaches apply only to facilities that manufacture semi-conductors but not to other processes in the lifecycle of these chemicals. Photoresists are comprised 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 with the exception of solvent compounds.

How this document was developed

This emission scenario document supercedes EPA's 1994 Generic Scenario for Semiconductors/ Photolithography (1). It has been developed using recent data on the semiconductor manufacturing industry, including process descriptions, operating information, chemicals used, wastes generated, waste treatment, worker activities, and exposure information. Specific sources of current information include U.S. Semi-Conductor Industry Association (SIA), Kirk-Othmer Encyclopedia of Technology, the US Census Bureau's County Business Patterns (CBP) Annual Survey of Manufacturers website, the Administrative Record for the Effluent Limitations Guidelines and Standards for the Metal Products and Machinery Point Source Category (MP&M), and the International Semiconductor Environmental Safety and Health Conference (ISESH). Data gathered during a site visit to a semiconductor manufacturing facility was also incorporated. References cited in this document are presented in Section 6. Additional references found but not cited in this document are listed in Appendix C.

In estimating environmental releases, this scenario assumes that the non-solvent portion of the photoresist is not volatile. It also assumes that releases to air from the handling of materials with a vapor pressure less than 0.01 torr are negligible and that inhalation exposure is not likely for liquids

with a vapor pressure less than 0.001 torr (2). This scenario describes methods to estimate the following parameters relevant to releases of and exposures to a photoresist chemical used in semiconductor manufacturing:

- Release amount from transport container residue;
- Release amount from equipment cleaning;
- Release amount from dispensed photoresist that does not adhere to the wafer;
- Release amount from developing the wafer;
- Release amount from etching and stripping of wafer;
- Number of sites applying photoresists and duration of activities;
- Number of workers that come into contact with photoresists; and
- Dermal exposures to photoresist chemicals from the photolithography process.

Process descriptions from other semiconductor manufacturing steps such as thin film deposition or doping have been included in Appendix A of this document to provide background information on the entire semiconductor manufacturing process. There are no releases of or exposures to the non-solvent components of the photoresists during these steps. Since 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. The estimation methods included within this scenario are applicable to any photoresist chemicals, regardless of their function within the photoresist formulation.

The draft document submitted by the US was circulated to the OECD member countries in December 2002. Comments were received from Canada, Germany and the Netherlands These comments and additional input from U.S. industry have been incorporated into this document. The approaches used in the main body of this scenario are based on U.S. data. Data supplied by German industry were reviewed and found to be comparable to those of the U.S. The scope of the scenario is designed to serve the needs of both the U.S. Environmental Protection Agency (EPA) and OECD, so in addition to providing approaches for estimating emissions or releases, this scenario also contains approaches for estimating occupational exposures. Because occupational exposures are not typically included in OECD Emission Scenario Documents (ESDs), the approaches for assessing occupational exposures may not have been included in the review process for most OECD member countries.

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1. INDUSTRY SUMMARY AND BACKGROUND

1. 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 heat or 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 (3).

2. The semiconductor manufacturing process involves many steps, requiring a wide range of chemicals. 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 (4).

3. The silicon wafer is the building foundation for semiconductors. These wafers are formed by chemically polishing and grinding a crystal ingot made from polycrystalline silicon until it has a mirror-like luster. Constructing the transistor on the wafer is accomplished through the following steps:

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

- Photolithography: A pattern is created on the wafer using photoresist chemicals. Releases of photoresist chemicals occur during the photolithography steps of photoresist application and developing.

- Doping: Doping processes are typically performed by diffusion or ion implantation techniques and introduce impurities to the wafer to alter the properties of the integrated circuit.

- Thin Film Deposition: Thin layers of various silicon-based chemicals are deposited to provide desirable properties or to serve as a mask for a particular sector of the wafer. A mask protects one area of the wafer while work is performed on another portion.

- Etching - Chemically remove 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.

- Metallization - 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, and chemical vapor deposition.

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

4. Cleaning, a process in which the wafer is cleaned in a solution to remove the various contaminants that may affect the final integrated circuit's electrical performance, is performed as part of several of the above mentioned steps. Semiconductor manufacturing is an iterative process in which these steps, with the exception of oxidation, are repeated to create layers on wafers.

5. During the photolithography step, a light-sensitive photoresist is applied to the wafer via a spin coating process. The spin coating process involves spinning the wafer at high speed on a vacuum chuck

to coat the wafer surface uniformly. A typical photoresist contains between 15 and 40% solids[1] suspended in a solvent-based chemical (5). This scenario does not address the solvent-based chemical portion of photoresists.

6. There are two types of photoresists, positive and negative, used in the photolithography process. Positive photoresists are typically comprised of a photoactive compound, resins, stabilizers, polymerization inhibitors, a viscosity control agent, dyes, plasticizers, and solvents (6). Chemical components of negative photoresists typically include a non-photo sensitive compound, a photosensitive material, a viscosity control agent, dyes, and solvents (5). Positive photoresists are the most common type used by industry (7). Some examples of chemicals currently used as photoresists are: polyalkylaldehyde, isoprene, and polymethacrylate.

7. After spin coating is complete, the wafer is soft-baked to remove most of the solvent in the photoresist. The solid component of the resist remains on the wafer and is exposed to light in a specific pattern. The wafer is then hard-baked to strengthen the photoresist remaining on the wafer. A developer solution is used to remove photoresist from the wafer in the given pattern. A more detailed description of the basic processing steps for manufacturing semiconductors is provided in Appendix B.

Number of Sites:

8. According to the U.S. Census Bureau's County Business Patterns (CBP) (8) for 2001, 1,177 establishments were in the North American Industry Classification System (NAICS) code 334413, which covers the Semiconductor & Related Devices Manufacturing industry sector. Table 1-1 provides the distribution of establishments based on the total number of workers at each establishment.

Table 1-1: Number of U.S. Establishments by Employment-Size Class for the Semiconductor & Related Devices Manufacturing Industry Sector (NAICS Code 334413)

Number of Employees	1-4	5-9	10-19	20-49	50-99	100-249	250-499	500-999	∃1000	Total Establishments
Number of Establishments	318	136	143	191	111	115	60	49	54	1,177*

*According to SIA, since the establishments encompass design centers, sales offices and warehouses as well as chip manufacturing establishments and since "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. The total number of chip manufacturing establishments would then be 389.

Number of Workers:

9. The CBP also indicates that 225,078 employees in 2001 were working in the NAICS code 334413 industry sector (8). According to the most recent data available from the Annual Survey of Manufacturers (ASM) (9) for the Electronic Components and Accessories sector (NAICS code 334413), 54% of all employees in 2000 were production workers. Using the CBP and ASM data, it can be estimated that 121,543 (225,078 H 0.54) workers are involved in the actual production of semiconductors[2]. By dividing the total number of production workers by the number of sites (121,543 / 1,177) it can be calculated that each site had, on average, 104 production workers. Each site would have,

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

[2] The ASM provides data for production workers for each NAICS code. For purposes of estimating the production worker population for the Semiconductor and Related Device Manufacturing industry sector, the percentage of production workers in the Semiconductor and Related Device Manufacturing industry sector from 2000 was used to calculate production employees using 2001 census data.

on average, 312 production workers if all establishments with less than 50 employees were not taken into account.

10. At a typical site, the production workers are the employees who work on manufacturing the semiconductors in clean room environments. Only a few of these workers will come into contact with the photoresist chemicals. In most factories, the process area of the equipment is a separate containment from the other clean areas of the factory or a "mini environment" exists to further control the process area. Based on a visit to a semiconductor manufacturing facility, it is estimated that an average of 20 to 25 workers per facility routinely handle the photoresist chemicals and therefore may be exposed (10).

2. PROCESS DESCRIPTION

11. The following process descriptions, figures, and tables are based on the following sources: U.S. Emergency Planning and Community Right-to-Know Act Section 313 Reporting Guidance for Semiconductor Manufacturing (11), EPA Office of Compliance Sector Notebook Project Profile of the Electronics and Computer Industry (3), and the Semiconductor Industry Association (SIA). The manufacture of a semiconductor chip involves several basic processes (see Figure 2-1):

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

12. The cleaning process, as noted in the Industry Summary and Background, is performed as part of several of these operations. The semiconductor manufacturing is an iterative process as shown in Figure 2-1. The steps bulleted above are repeated to create layers on wafers. (23)

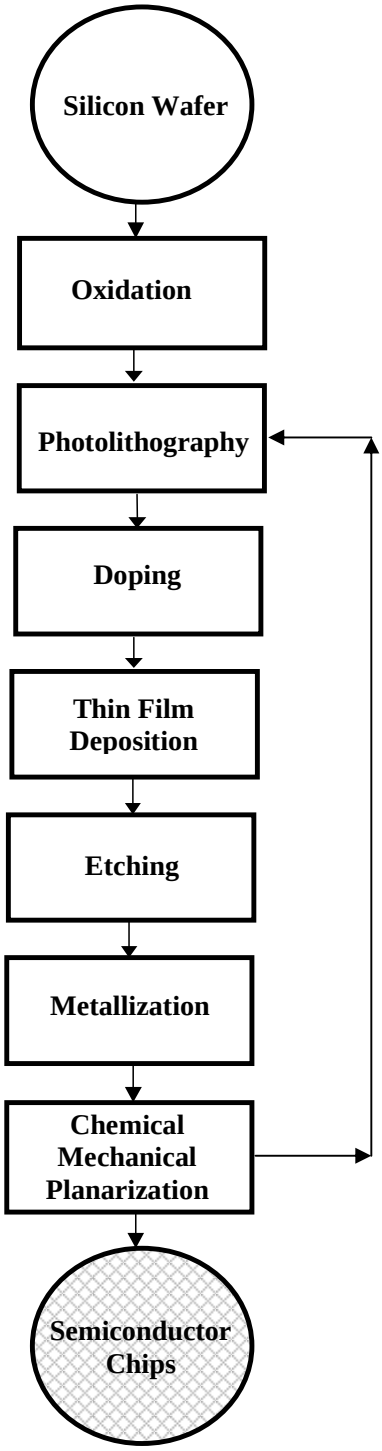
13. The primary component of a semiconductor is the wafer, or chip. Silicon has traditionally been the substrate used to manufacture semiconductors; recently, other materials such as gallium arsenide (GaAs) and indium phosphide (InP) have been used as substrates.

14. The semiconductor manufacturing process is continually evolving. The variety of distinct processing steps involved results in a range of processes that may occur at a single plant or in varying processes 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.

15. A clean environment is essential to the manufacture of semiconductors; thus many of the process steps are conducted in a clean room and cleaning operations precede and follow many of the manufacturing process steps. Wet processing, during which semiconductor devices are repeatedly immersed in or sprayed with solutions, is commonly used to minimize the risk of contamination.

16. Through the use of these physical and chemical processes, hundreds of thousands of miniature transistors are created on the wafer. The following subsections describe typical operations, chemicals used, and potential release points during the photolithography and etching steps.

Figure 2-1. Overall Process Flow Diagram - Semiconductor Manufacturing[3]



2.1 Primary Semiconductor Manufacturing Steps with Photoresist Releases

17. The two primary semiconductor manufacturing steps that potentially release photoresist are photolithography and etching. The photolithography process includes application, soft bake, image application, hard bake, and developing while the etching process includes etching and stripping. A flow diagram, including potential release points, for the photolithography and etching steps is presented in Figure 2-2.

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

2.1.1 Photolithography

18. 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.

Photoresist Application

19. In this process, photoresist is applied to the wafer on a spin track. Photoresist chemicals are polymer-based liquids in which photoactive molecules are dissolved in a carrier solvent (5). A fixed amount of photoresist is metered onto the wafer, which is then 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 of the photoresist applied to the wafer remains on the wafer as the surface coating.

20. Photoresists are 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 base resins, organic carrier solvents, stabilizers, viscosity control agents, dyes, plasticizers, and photosensitive compounds (5).

- *Negative* photoresists are chemicals that polymerize and stabilize upon exposure to radiation. The developing process removes the photoresist that was protected from radiation. Polyisoprene is present in many negative photoresists. These photoresists consist of photosensitive compounds, non-photosensitive compounds, viscosity control agents, dyes, and carrier solvents. Negative photoresists use azides for photosensitive compounds (5).

21. 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% solids[4] suspended in a solvent-based chemical (5). Typical chemicals used in photolithography are listed in Table 2-1.

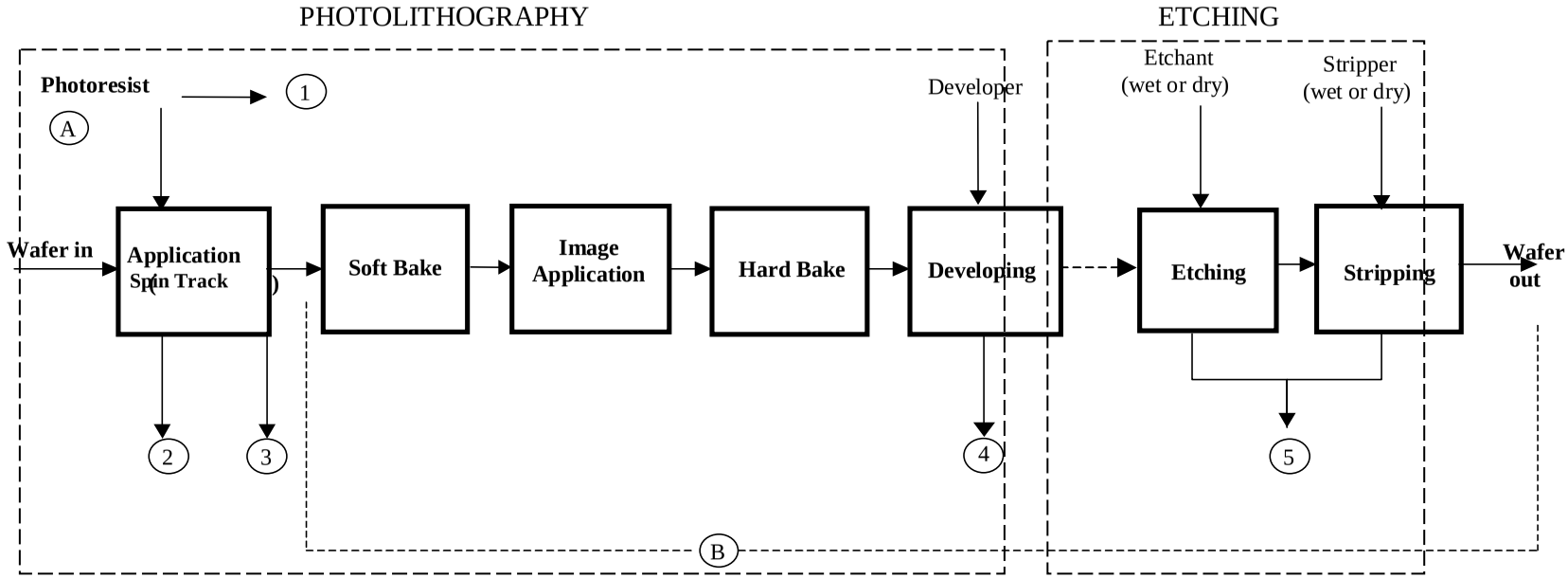
22. To remove the solvent, a pre-expose bake or Asoft-bake@ process is used. The wafer is heated until the solvent evaporates and a uniform coat of photosensitive chemicals remains on the silicon wafer.

23. A pattern is introduced into the resist by exposing pre-defined areas of the wafer to light, lasers, or electron beams. 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 radiation. Radiation effects are dependent on whether a positive or negative photoresist is applied to the wafer.

24. Releases from application of the photoresist to the wafer include residual photoresist from container, equipment cleaning solution, and excess photoresist that was spun off the wafer.

[4] The Semiconductor Industry Association (SIA) indicates that 20% solids may be a reasonable average based on anecdotal information.

Figure 2-2: Flow Diagram for Photoresist Use and Release in Semiconductor Manufacturing



RELEASES OF PHOTORESIST CHEMICALS WITH DEFAULT VALUES:

(1) Release from container residue (defaults: 0.6% of input; to water or incineration or land)

(2) Release from equipment cleaning (defaults: 1% of remaining input; to incineration or land)

(3) Release from photoresist that does not adhere to the wafer during application (defaults: approx 92% of remaining input; to incineration)

(4) Release from photoresist removed during developing (defaults: 50% of remaining input; to water)

(5) Release from photoresist removed during the etching and/or stripping process (defaults: 100% of remaining input; to water or recycle)

EXPOSURES TO PHOTORESIST CHEMICALS:

(A) Potential dermal exposure from manual transfer of photoresist to application apparatus

(B) Potential dermal exposure from manual transfer of wafers from one process step to another in non-automated systems

Table 2-1 :Typical Chemicals Used in the Photolithography Process for Semiconductor Manufacturing (12)

Photoresists	**Developer**	**SOLVENTS AND CLEANING AGENTS**
Positive: Ortho-diazoketone Polymethacrylate Polyfluoroalkylmethacrylate Polyalkylaldehyde Polycyanoethylacrylate Polymethylmethacrylate Poly (hexafluorobutylmeth-acrylate) 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

Photoresist Developer

25. The wafer is exposed to developer solution to dissolve the unwanted portion of the photoresist chemical, yielding a stencil for further processing steps. The number of photolithography steps required depends on the type of integrated circuit that is being produced.

26. Releases from the developing process include developer container residue and the developer bath. The container residue is expected to consist only of developer solution and not photoresist. The developer bath will contain the photoresist chemicals removed in this process.

2.1.2 Etching

Wafer Etching

27. Etching is used to chemically remove 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 processes usually occur after a photoresist pattern has been applied, so that the etching is accomplished in specific areas.

28. Etching may be performed using solutions of acids, bases, or oxidizers (wet etching), or by using various gases (usually halogenated) in a plasma environment (dry etching). During wet etching, acid solutions are used to 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.

29. 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.

30. The main source of releases from etching activities is the etchant material itself, either the inorganic acids used in wet etching processes, or certain halogenated organic compounds used in dry etching processes. The etching solution will also contain the film removed from the wafer, including photoresist.

Photoresist Stripping

31. Residual photoresist may remain on the wafer after etching. Residual photoresist is removed using stripping. There are two types of stripping that may be used in the process, wet or dry. Wet stripping uses a wide variety of chemical resist strippers (solvents, acids, bases, etc.) to dissolve the photoresist. Dry stripping uses plasma gas, which reacts with the photoresist, yielding gases that may be removed with a pump. Selectivity of the stripping material to be used is important to ensure the base material of the wafer is not removed.

32. Releases from the stripping process can include stripper container residue and the stripping bath. The container residue will consist only of stripping solution and not photoresist. The stripping bath will contain all photoresist that remained on the wafer.

3. SCREENING LEVEL ESTIMATION TECHNIQUES/METHODS

33. This generic scenario focuses on the non-solvent portion of photoresist chemicals used in the semiconductor manufacturing process. The key steps in which photoresists are used and released include photoresist application, pre-expose bake, image application, post-expose bake, developing, etching, and stripping. This section presents general facility calculations, release assessments and occupational exposure assessments. The general facility calculations estimate daily use rates of photoresist and of the chemical of interest, number of sites using the chemical of interest, and number of days of use. The release assessment provides estimates and media of release for each release source and the occupational exposure assessment estimates the number of workers and the level of exposure. The default values cited in this section of the scenario are intended to be used when site-specific or industry-specific information or data is not available.

34. Because there are several available estimates of some parameters, the user should consider how the choices of these parameters may affect final assessment results. If conservative estimates of release amounts are sought, the most conservative daily use rates should be used. For the remainder of this generic scenario, parameter values are chosen to estimate conservative release amounts.

3.1 General Facility Calculations

35. Some general facility parameter estimates are important for release estimation. Several of these parameters include daily use rates of the photoresist and of the chemical of interest, number of days of photoresist application, and numbers of sites using photoresists containing the chemical of interest. The general facility estimates presented in this section are based on the following key assumptions from recent information gathered in the U.S. (26):

- A facility applies photoresists to wafers at a rate of 100 to 1000 times per hour
- A facility applies photoresists to wafers for 20 to 24 hours per day
- A facility applies photoresists to wafers at a rate of 0.5 to 5 mL per application (23, 26)
- A facility applies photoresists to wafers for 250 to 360 days per year

36. The 1997 MacCentral edition of AUnder the Hood@ reviewed the photolithography process and found that Aa few millimeters of photoresist are dropped onto the center of the wafer with a dropper or syringe-like delivery system@ (14).

37. Default values used for general facility estimates, accompanied by their references, are provided in Table B-2 of Appendix B.

Daily Use Rate of Photoresist [Q_{photo_day} (kg/site-day)] and Number of Days of Photoresist Application: [$TIME_{apply\_days}$(days/yr)]:

38. The amount of photoresist used per day at a semiconductor manufacturing facility depends primarily upon the number of photoresist applications to wafers per hour, the amount of photoresist applied per application, and the number of application hours per day. Equation 3-1 expresses this estimation method, and Table 3-1 shows a range of parameter values and associated estimated use rates. The conservative average photoresist use rate of 36 kg/site-day from Table 3-1 is used as a default value in equation 3-2 for estimating the average daily use rate of the chemical of interest (Q_{chem_day}), which is a key parameter used in the release estimation equations.

$$Q_{photo\_day} = N_{apply} \times TIME_{apply\_hours} \times Q_{apply} \times RHO_{photo} / 1000 \qquad \text{(Eqn. 3- 1)}$$

Where:

Q_{photo_day}	=	Average daily use rate of the photoresist per facility (kg/site-day)
N_{apply}	=	Number of applications per hour and site (applications/site-hr)
$TIME_{apply\_hours}$	=	Hours of application per day (hr/day)
Q_{apply}	=	Quantity of photoresist applied per wafer application (mL/application)
RHO_{photo}	=	Photoresist density (g/mL) (Default = 1)

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

40. Although each parameter in Eqn. 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. Several example facilities are shown in Table 3-1 below.

Table 3-1: Parameters and Values for Daily and Annual Photoresist Use Rate Calculation (26)

Manufacturing Scale	N_{apply}	$TIME_{apply\_hours}$	Q_{apply}	Q_{photo_day}	$TIME_{apply\_days}$	Q_{photo_yr}
	(applications/ site-hr)	(hours/day)	(ml/application)	(kg/ site-day)	(days/yr)	(kg/ site-yr)
Niche	100	20	5	10	250	2,500
Large Scale	500	22	3	33	300	9,900
Large Scale	1,000	24	1.5	36	360	12,960

Table Note: 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). Large scale is 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 applied/application and the range of operating characteristics (hrs/day, days/year). Applications/hr/site is the product of wafer starts/hr/site and applications/wafer start. Applications/hr/site, hours of operation/day, and days of operation/year are typically higher for newer large facilities. Photoresist applied/application is typically lower for newer large facilities.

41. Days of photoresist application per year ($TIME_{apply\_days}$) must be associated appropriately with daily use rate [Q_{photo_day} (kg/site-day)] to reflect the total annual use rate. The annual facility use rate of photoresist [Q_{photo_yr} (kg/site-yr)] in Table 3-1 is calculated by multiplying the daily use rate of photoresist by the number of application days per year [$TIME_{apply\_days}$ (days/yr)].

Daily Use Rate of Chemical of Interest [Q_{chem_day} (kg/site-day)]:

42. To estimate the throughput of the chemical of interest that is a component of photoresist, multiply by the chemical's concentration (weight fraction) in the photoresist. Also, facilities use multiple photoresists. The chemical of interest may not be in all of these photoresists. If appropriate, a correction factor could be applied to adjust throughput (e.g., (estimated number of photoresist applications containing the chemical of interest per wafer)/(average number of photoresist applications per wafer)). If chemical

specific information is not available or not known, the conservative default value for this correction factor is 1.

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

Where:

Q_{chem_day} = Daily use rate of chemical of interest chemical (kg/site-day).

Q_{photo_day} = Daily use rate of photoresist at each facility (kg/site-day) (default: 36 from Table 3-1).

F_{chem} = Fraction of chemical of interest in photoresist (if specific information is not provided, default = 0.4; reference range is 0.4 (5)) (German industry and SIA suggest 0.2 (24, 23))

N_{app_chem} = Number of photoresist applications per wafer containing the chemical of interest (applications/wafer). Default: Napp_chem = Napp_photo

N_{app_photo} = Average number of photoresist applications per wafer (applications/wafer)

Number of Sites (N_{sites}):

43. The number of semiconductor manufacturing facilities using the photoresist that contains the chemical of interest (N_{sites}) depends on the total production of the chemical of interest (Q_{chem_yr}), which must be adjusted by container residual ($F_{container\_disp}$), the daily use rate of the chemical of interest (Q_{chem_day}), and the annual operating days ($TIME_{apply\_days}$).

44. Equation 3-3 shows how to determine the number of semiconductor manufacturing facilities estimated to use the photoresist that contains the chemical of interest.

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

Where:

N_{sites}[5] = Number of semiconductor manufacturing facilities using the photoresist that contains the chemical of interest

$F_{container\_disp}$ = Fraction of photoresist residue in containers (default = 0.006) (19) (see Section 3.2.1 below)

Q_{chem_yr} = Production volume of the chemical of interest (kg/yr)

Q_{chem_day} = Daily use rate of chemical of interest (kg/site-day)

$TIME_{apply\_days}$ = Days of photoresist application per year (days/yr) (default: 360 (Table 3-1))

[5] If N_{sites} is calculated to be less than one using equation 3-3, then N_{sites} should be assumed to be one and $TIME_{apply\_days}$ should be recalculated using the following equation:

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

3.2 Release Assessments

45. This section presents approaches for calculating the amount of photoresist chemicals released for each release source. The release sources are discussed in the order that they occur in the process (please refer to flow diagram in Figure 2-2). An indication of the most likely media of release (air, water, landfill, incineration) is also provided. The primary sources of releases include container residue, process equipment cleaning, photoresist that does not adhere to the wafer in the application process, spent developer, and spent etching and stripping solutions. Key default values used for release and exposure estimates, accompanied by their respective references, are provided in Table B-2 of Appendix B.

46. All release equations below 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.

47. This scenario 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.

3.2.1 Container Residue

48. Photoresist is typically supplied to the user in small containers, including 1-gallon (4-liter) bottles and 2.5-gallon (10-liter) NOW Pack bottles with a collapsible internal bladder (1, 18). Potential releases occur from cleanout and/or disposal of the used container. This scenario assumes that up to 0.6% of the liquid originally in small containers remains as residual after unloading (19). The media of release for this source is uncertain. For cases where the media of release is uncertain, it is assumed that disposal may be to water, land, or incineration (25).

49. The daily release rate of the photoresist chemical of interest (kg/site-day) can be calculated using equation 3-4. At the default daily use rate of photoresist of 36 kg/site-day (Table 3-1), there are multiple bottles used per day. For this reason, the release rate is daily and the fractional loss rate may be applied to the daily use rate.

$$Elocal_{container\_residure\_disp} = Q_{chem\_day} \times F_{container\_disp} \qquad \text{(Eqn. 3-4)}$$

Where:

$Elocal_{container\_residue\_disp}$ = Daily release of chemical of interest from container residue (kg/site-day)

Q_{chem_day} = Daily use rate chemical of interest (kg/site-day)

$F_{container\_disp}$ = Fraction of photoresist residue in container to incineration or landfill (default = 0.006) (19)

This release rate is applicable over $TIME_{apply\_days}$ (default: 360 (Table 3-1)) for N_{sites}.

3.2.2 Residual from Equipment Cleaning

50. Most facilities use various solvents to clean process equipment (17). As a default, it is assumed that 1% of the daily use rate of photoresist, and therefore also of the chemical of interest, less the container residue, is released from cleaning (17, 19, 23). This release is expected to be sent to incineration or landfill (23).

51. The daily release rate of the photoresist chemical of interest (kg/site-day) can be calculated using equation 3-5.

$$Elocal_{equip\_disp} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times F_{equip\_disp} \quad \text{(Eqn. 3- 5)}$$

Where:

$Elocal_{equip\_disp}$ = Daily release of chemical of interest from equipment cleaning (kg/site-day)
Q_{chem_day} = Daily use rate of chemical of interest (kg/site-day)
$F_{container\_disp}$ = Fraction of photoresist residue in container (default = 0.006) (19)
E_{equip_disp} = Fraction of photoresist residue in equipment (default = 0.01) (17, 19, 23)

This release rate is applicable over $TIME_{apply\_days}$ (default: 360 (Table 3-1)) for N_{sites}.

3.2.3 Application Excess (Spin-off)

52. 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, typically to incineration (23). This generic scenario assumes that a default range of 1% to 7% of the dispensed photoresist containing the chemical of interest remains on the wafer (17, 23), and that the remaining "spun-off" material is disposed. Some of this excess photoresist remains in the equipment and is disposed as cleaning residue, and this amount is excluded from the application excess.

53. The daily release rate of the photoresist chemical of interest (kg/site-day) can be calculated using equation 3-6.

$$Elocal_{excess\_disp} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times \left(1 - F_{photo\_wafer}\right) \quad \text{(Eqn. 3- 6)}$$

Where:

$Elocal_{excess\_disp}$ = Daily release of chemical of interest from application excess (kg/site-day)
Q_{chem_day} = Daily use rate of chemical of interest (kg/site-day)
$F_{container\_disp}$ = Fraction of photoresist residue in container (default = 0.006) (19)
E_{equip_disp} = Fraction of photoresist residue in equipment (default = 0.01) (17,19)
F_{photo_wafer} = Fraction of the dispensed photoresist that adheres to the wafer (default = 0.01 to 0.07) (17, 23)

This release rate is applicable over $TIME_{apply\_days}$ (default: 360 (Table 3-1)) for N_{sites}.

3.2.4 Residual in Developer

54. Developer solutions are a potential source of release of the chemical of interest (17). The developer solution is designed to remove either the exposed (positive) or unexposed (negative) photoresist from the wafer. The developer with removed photoresist is expected to be released to water (23). It is estimated that 50% of the photoresist adhered to the wafer is removed in the development process (20). Some of this photoresist remains in the equipment and is disposed as cleaning residue, and this amount is excluded from the loss from this source.

55. The daily release rate of the photoresist chemical of interest (kg/site-day) can be calculated using equation 3-7.

$$Elocal_{developer} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{photo\_wafer} \times F_{photo\_develop}$$

(Eqn. 3- 7)

Where:

$Elocal_{developer}$	=	Daily release of chemical of interest from developing (kg/site-day)
Q_{chem_day}	=	Daily use rate of chemical of interest (kg/site-day)
$F_{container\_disp}$	=	Fraction of photoresist residue in container (default = 0.006) (19)
E_{equip_disp}	=	Fraction of photoresist residue in equipment (default = 0.01) (17,19)
F_{photo_wafer}	=	Fraction of photoresist that adheres to wafer (default = 0.01 to 0.07) (17, 23)
$F_{photo\_develop}$	=	Fraction of photoresist removed in development (default = 0.5)[6] (17)

This release rate is applicable over $TIME_{apply\_days}$ (default: 360 (Table 3-1)) for N_{sites}.

3.2.5 Residual in Etching and Stripping

56. Etching the wafer and application of stripping solution follows the development of the wafer in the photolithography process, and these processes remove the remainder of the photoresist from the wafer after the developing process. Etching is used to selectively remove metal from the wafer. The etching solution 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 or recycle (23). Some of this photoresist remains in the equipment and is disposed as cleaning residue, and this amount is excluded from the loss from this source.

57. The daily release rate of the photoresist chemical of interest (kg/site-day) can be calculated using equation 3-8.

$$Elocal_{etch\_strip\_disp} = Q_{chem\_day} \times F_{photo\_wafer} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times \left(1 - F_{photo\_develop}\right)$$

(Eqn. 3- 8)

Where:

$Elocal_{etch\_strip\_disposal}$	=	Daily release of chemical of interest (kg/site-day)
Q_{chem_day}	=	Daily use rate of chemical of interest (kg/site-day)
$F_{container\_disp}$	=	Fraction of photoresist residue in container (default = 0.006) (19)
E_{equip_disp}	=	Fraction of photoresist residue in equipment (default = 0.01) (17,19)
F_{photo_wafer}	=	Fraction of photoresist that adheres to wafer (default = 0.01 to 0.07) (17, 23)
$F_{photo\_develop}$	=	Fraction of photoresist removed in developing **(**default = 0.5) (17)

[6] German Industry comments to the September 2002 version states the following: "[O]nly 4% of the photoresist remains on the wafer. After irradiation, about 2% is polymerised and 2% is not developed and removed by a solvent."

This release rate is applicable over $TIME_{apply\_days}$ (default: 360 (Table 3-1)) for N_{sites}.

3.3 Occupational Exposure Assessments

58. Because semiconductors must be kept free of dust and other contaminants, most manufacturing facilities use clean rooms where workers are required to wear various personal protective equipment to maintain the integrity of the clean room. The methods that serve to protect the worker from contaminating the clean room and the product also serve to protect the worker from exposure to any chemicals used in the process conducted in the clean room. In addition, most of the process is conducted in a closed system, which results in limited worker exposure to the photoresist chemicals (i.e., only when opening and closing equipment to transfer materials).

59. Worker activities in the process involve the transfer of the photoresist to the application apparatus and the transfer of the wafer from one apparatus used in the process to another. Each wafer is cleaned prior to photolithography processing by placing it into solutions of acetone and trichloroethylene. The process is typically automated; however, workers may manually place the wafer into these solutions, then transfer the wafer to the spin-coat apparatus where photoresist chemical is added to the wafer. After spinning, some resist chemical may remain on the spin-coat apparatus and must be cleaned. The workers may also transfer the photoresist-covered wafers to other processing steps throughout the manufacturing process.

3.3.1 Number of Workers Exposed Per Site

60. Each semiconductor facility usually operates two shifts per day (16). Information obtained from the County Business Pattern Data and the Annual Survey of Manufacturers for a broad SIC code yield 104 production workers per site[7]. Based on a site visit to a semiconductor manufacturing facility, EPA estimates that on average a total of 20 to 25 workers per facility could potentially come into contact with the photoresist chemicals each day, and therefore may be exposed (19). The information obtained from the site visit is believed to provide a better estimate than the County Business Pattern (CBP) data. Therefore, 20 to 25 workers per facility may be assumed as a default.

3.3.2 Inhalation

61. Because clean rooms and enclosed equipment are used during the production process, non-volatile chemicals of interest in photoresists are not expected to be airborne in workers' breathing zones. Therefore, inhalation exposures are not expected.

3.3.3 Dermal

62. Workers may come into direct contact with the chemical of interest while transferring the photoresist to the application apparatus (i.e., changing bottles) and in limited cases of manual transferring of wafers to and from operations if the correct personal protective equipment is not worn. To estimate dermal exposure to the chemical of interest during these activities, the EPA/OPPT incidental one-hand contact with liquids model should be used (21). This estimation approach is based on experimental data from a study that measured the amount of materials remaining on the skin after various degrees of exposure. Additional data measuring amounts of dermal exposure during industrial activities were also used to develop the dermal model. The following key assumptions and limitations of the dermal model apply to the use of the model. First, it is assumed that no dermal protection is used to limit exposure.

[7] The production workers per site is 389 if all facilities under 50 employees are not taken into account since according to SIA facilities with less than 50 employees could not support semiconductor manufacturing.

Also, one incident per day ($N_{exp\_incident}$ = 1) is assumed because the quantity of liquid remaining on skin (Q_{liquid_skin}), with few exceptions, is not expected to be significantly affected either by wiping excess from skin or by repeated contact(s) with additional chemical (i.e., wiping excess from the skin does not remove a significant fraction of the small layer of chemical adhering to the skin and additional contacts with the chemical 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.

63. The daily potential dose rate is estimated in Equation 3-9.

$$EXP_{dermal} = AREA_{surface} \times Q_{liquid\_skin} \times F_{chem} \times N_{exp\_incident} \quad \text{(Eqn. 3-9)}$$

Where :

EXP_{dermal} = Potential dermal exposure (mg/day)
$Area_{surface}$ = Surface area of contact (default = 420 cm^2, 1 hand (21))
Q_{liquid_skin} = Quantity of liquid remaining on skin (defaults = 2.1 mg/cm^2 – incident (high-end) and 0.7 mg/cm^2 –incident (low-end) (21))
F_{chem} = Fraction of chemical of interest in photoresist (if specific information is not provided, default = 0.4; reference range is 0.4 (5)) (German industry and SIA suggest 0.2 (24, 23))
$N_{exp\_incident}$ = Number of exposure incidents per day (default = 1 incident/day)

Workers may be exposed at this level for up to 250 days per year. If the number of application days ($TIME_{apply\_days}$) is less than 250, then assume the days per year exposure to be up to $TIME_{apply\_days}$.

4. SAMPLE CALCULATIONS

64. This section presents an example of the use of all of the equations introduced in Section 3 of the document. The hypothetical operating scenario presented displays how the equations in Section 3 might be used to estimate releases of and exposures to a non-solvent chemical found in photoresist formulations. The default values used in these calculations are presented in Section 3 and should be used only in the absence of site-specific information. The following assumptions are made in this example calculation.

Given/ known data:

Chemical of interest production volume ($Q_{chem\_yr)}$ is 5,000 kg/yr
Chemical of interest is 15% by weight in the photoresist formulation (F_{chem}).

Daily Use Rate of Photoresist [Q_{photo}] kg/site-day]:

No site-specific information and data for Eqn. 3-1 parameters (N_{apply}, $TIME_{apply\_hours}$, and Q_{apply}) are given or known for the daily photoresist use rate calculation. Therefore, scenario defaults are appropriate. Use the conservative value of $Q_{photo\text{-}day}$ and the associated $TIME_{apply\_days}$ for Large Scale Manufacturing from Table 3-1. Then, the following values will be used for the assessment.

$Q_{photo\text{-}day}$ = 36 kg/site-day;
$TIME_{apply\_days}$ = 360 days/yr.

Daily Use Rate of Chemical of Interest Use Rate of Photoresist [Q_{chem_day}, kg/site-day]:

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

$$Q_{chem\_day} = \frac{36\ kg}{site\text{-}day} \times 0.15 \times \frac{1}{1} = \frac{5.4\ kg}{site - day}$$

Number of Sites [N_{sites}]:

$$N_{sites} = \frac{\left(1 - F_{container\_disp}\right) \times Q_{chem\_yr}}{Q_{chem\_day} \times TIME_{apply\_days}} = \frac{(1 - 0.006) \times \frac{5{,}000\ kg}{yr}}{\left(\frac{5.4\ kg}{site - day} \times \frac{360\ day}{yr}\right)} = 5.1 sites \qquad \text{(Eqn 3-3)}$$

Container Residue Releases:

$$Elocal_{container\_residure\_disp} = Q_{chem\_day} \times F_{container\_disp} \qquad \text{(Eqn. 3-4)}$$

$$Elocal_{container\_residue\_disp} = \frac{5.4\ kg}{site\text{-}day} \times 0.006 = \frac{0.032\ kg}{site\text{-}day}$$

Media of Release: water, land, or incineration (default)

Equipment Cleaning Releases:

$$Elocal_{equip\_disp} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times F_{equip\_disp} \quad \text{(Eqn. 3-5)}$$

$$Elocal_{equip\_disp} = 5.4 \frac{kg}{site - day} \times (1 - 0.006) \times 0.01 = 0.054 \frac{kg}{site - day}$$

Media of Release: land or incineration (default)

Application Excess (Spin-off):

$$Elocal_{excess\_disp} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times \left(1 - F_{photo\_wafer}\right) \quad \text{(Eqn. 3-6)}$$

$$Elocal_{excess\_disp} = 5.4 \frac{kg}{site - day} \times (1 - 0.006) \times (1 - 0.01) \times (1 - 0.01 \text{ to } 0.07) = 4.9 \text{ to } 5.3 \frac{kg}{site - day}$$

Media of Release: incineration (default)

Developer Residual:

$$Elocal_{developer} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{photo\_wafer} \times F_{photo\_develop} \quad \text{(Eqn. 3-7)}$$

$$Elocal_{developer} = \frac{5.4\ kg}{site - day} \times (1 - 0.006) \times (1 - 0.01) \times (0.01 \text{ to } 0.07) \times 0.5 = \frac{0.027\ kg}{site - day}$$

Media of Release: water (default)

Spent Etching and Stripper Solution:

$$Elocal_{etch\_strip\_disp} = Q_{chem\_day} \times F_{photo\_wafer} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times \left(1 - F_{photo\_develop}\right) \quad \text{(Eqn. 3-8)}$$

$$Elocal_{etch\_strip\_disp} = \frac{5.4\ kg}{site - day} \times (0.01 \text{ to } 0.07) \times (1 - 0.006) \times (1 - 0.01) \times (1 - 0.5) = \frac{0.027\ kg}{site - day}$$

Media of Release: water (default)

Inhalation Exposure:

Negligible (VP < 0.001 torr)

Dermal Exposure in the absence of personal protective equipment:

$$EXP_{dermal} = Area_{surface} \times Q_{liquid\_skin} \times F_{chem} \times N_{exp\_incident} \quad \text{(Eqn. 3-9)}$$

$$EXP_{dermal} = 420\ cm^2 \times \frac{2.1\ mg}{cm^2 - incident} \times 0.15 \times \frac{1\ incident}{day} = \frac{132\ mg}{day}$$

EXP_{dermal} applies to 20 to 25 workers per site (default) over up to 250 days/yr (default).

5. DATA GAPS/UNCERTAINTIES AND FUTURE WORK

65. Much of the data used for generating general facility estimates, release estimates, and exposure estimates are based on anecdotal data and information from various sources. This scenario could be improved by collecting measured data and associated information to verify or supercede the anecdotal data and information

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Appendix A: 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. By strictly governing the dopant ion momentum, this process allows for precise control of the penetration into the silicon substrate. The high kinetic energy of the ions during bombardment causes damage to 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 non-gaseous diffusion. In gaseous diffusion, dopant gases are introduced into the furnace to diffuse into the exposed areas of the substrate. Alternatively, in non-gaseous diffusion, the furnace heat will allow 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.

A process flow diagram of the doping processes is shown in Figure A-1, and examples of typical chemicals used and waste generated in the process are listed in Table A-1.

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 activities. 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 activities.

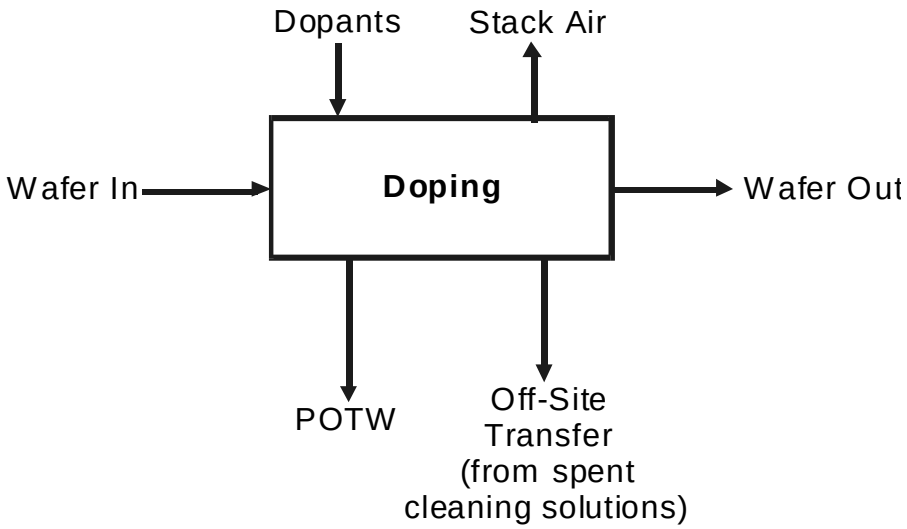

Figure A-1. Process Flow Diagram for Typical Doping Process

Table A-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

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.

A typical process flow diagram for the thin film deposition process is shown in Figure A-2. Typical chemicals used in the process are listed in Table A-2.

Thin film furnace or oxidation chamber exhaust (from venting of gas left unreacted after CVD process or from purging of the reactor and transport lines after the process is completed (13)) 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 (13). 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 clean room environment with no human intervention.

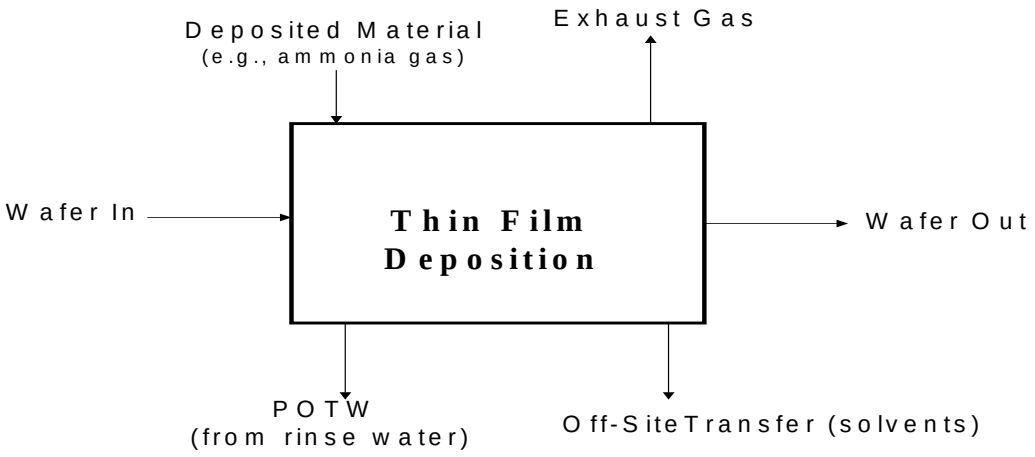

Figure A-2. Process Flow Diagram for the Thin Film Deposition Process

Table A-2: Materials Used and Waste Generated During Thin Film Deposition

Materials Used	Wastes 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

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 to selectively remove the top part of a non-conducting 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 removal 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.

A process flow diagram of the CMP processes is shown in Figure A-3. Spent slurry containing nitrates from the planarization process is typically transferred offsite to a POTW.

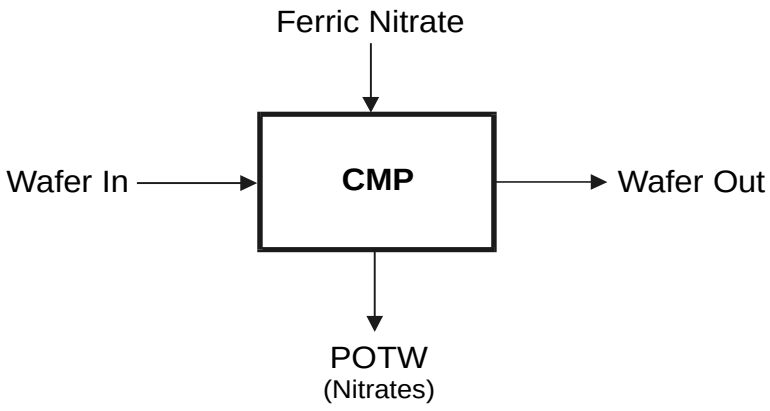

Figure A-3. Process Flow Diagram for Typical Chemical Mechanical Planarization Process

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.

A process flow diagram of the cleaning process is shown in Figure A-4, and examples of typical chemicals used and waste generated in the process are listed in Table A-3.

Waste solvents used in cleaning operations may be either directly discharged to surface water after on-site treatment or transferred offsite 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.

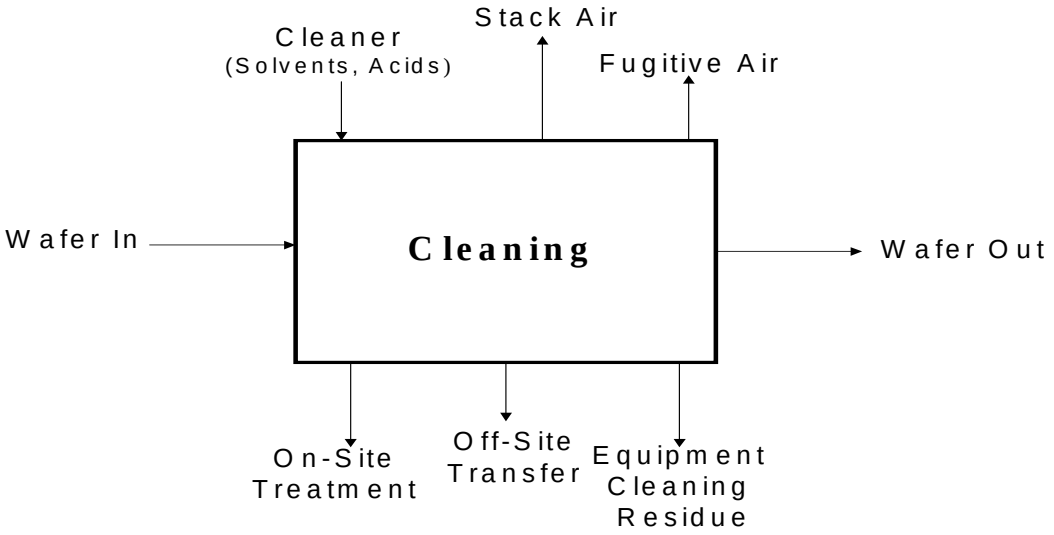

Figure A-4. Process Flow Diagram for Typical Cleaning Process

Table A-3: Cleaning Materials Used and Waste Generated During the Cleaning Process

Cleaning Materials Used	Wastes 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

*Added to this version per SIA suggestion

Appendix B: Estimation Equation Summary And Default Value Documentation

Summary of Release and Exposure Estimation Equations

Table B-1 summarizes the equations introduced in Section 3 of this document. These equations may be used in evaluating releases of and exposures to non-solvent photoresist chemicals used in the photolithography process. A description of each equation along with the supporting nomenclature is provided In Table BC-2.

Table B-1: Photoresist Use Release and Exposures Calculation Summary

General Facility Estimates
Operating Days per Year (days/year), $TIME_{apply\_days}$: A facility applies photoresists to wafers for 250 to 360 days per year. Default for conservative use rate is 360 days/yr. Refer to Table 3-1.
Operating Hours per Day (hours/day), $TIME_{apply\_hours}$: A facility applies photoresists to wafers for 20 to 24 hours per day. Default for conservative use rate is 24 hours/day. Refer to Table 3-1.
Daily Use Rate of Photoresist per Site (kg/site-day), Q_{photo_day}: $Q_{photo\_day} = N_{apply} \times TIME_{apply\_hours} \times Q_{apply} \times RHO_{photo} \div 1000$ (Eqn.3-1)
Daily Use Rate of Chemical of Interest (kg/site-day), 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, N_{sites}: $N_{sites} = \frac{\left(1 - F_{container\_disp}\right) \times Q_{chem\_yr}}{Q_{chem\_day} \times TIME_{apply\_days}}$ (Eqn. 3-3)

Release Calculations		
Source	**Possible Medium**	**Daily Release Rates (kg/site-day), Elocal (for Given Sources)**
Container Residue	Water Land Incineration	$Elocal_{container\_residure\_disp} = Q_{chem\_day} \times F_{container\_disp}$ (Eqn. 3-4)
Equipment Cleaning Residue	Land Incineration	$Elocal_{equip\_disp} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times F_{equip\_disp}$ (Eqn. 3-5)
Application Excess (Spin-off)	Incineration	$Elocal_{excess\_disp} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times \left(1 - F_{photo\_wafer}\right)$ (Eqn. 3-6)
Developer Residual	Water	$Elocal_{developer} = Q_{chem\_day} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times F_{photo\_wafer} \times F_{photo\_develop}$ (Eqn. 3-7)
Etching and Stripping Residual	Water	$Elocal_{etch\_strip\_disp} = Q_{chem\_day} \times F_{photo\_wafer} \times \left(1 - F_{container\_disp}\right) \times \left(1 - F_{equip\_disp}\right) \times \left(1 - F_{photo\_develop}\right)$ (Eqn. 3-8)

Occupational Exposure Calculations
Dermal Exposure in the absence of personal protective equipment (mg/day): $EXP_{dermal} = AREA_{surface} \times Q_{liquid\_skin} \times F_{chem} \times N_{exp\_incident}$ (Eqn. 3- 9)
Number of Workers Exposed Per Site: Default = 20 to 25 production workers/site (18)

Table B-2: Default Value Declaration and Documentation

Variable	Variable Description	Default Value	Data Source
$TIME_{apply\_days}$	Days of Photoresist application per year (days/yr)	360 (See Table 3-1)	(26)
$TIME_{apply\_hours}$	Hours of application per day (hr/day)	24 (See Table 3-1)	(26)
$AREA_{surface}$	Surface area of contact	420 cm^2, 1 hand	(21)
F_{chem}	Fraction of chemical of interest in photoresist	0.4 (conservative)	(5)
Q_{liquid_skin}	Quantity of Liquid Remaining on Skin per Incident (mg/cm^2-incident)	2.1 (high-end) 0.7 (what-if)	(21)
N_{apply}	Number of applications per hour and site (applications/site-hr)	1000 (See Table 3-1)	(26)
Q_{photo_day}	Daily Use Rate of Photoresist per Site (kg/site-day)	36 kg/site-day (See Table 3-1)	(26)
Q_{apply}	Quantity of photoresist applied per application (ml/application)	1.5 (See Table 3-1)	(26)
F_{photo_wafer}	Fraction of Photoresist that adheres to the wafer	0.01 to 0.07	(17, 23)
$F_{container\_disp}$	Fraction of photoresist residue in container	0.006 (smaller containers)	(19)
$F_{photo\_develop}$	Fraction of Photoresist on wafer removed in development	0.50	(17)
F_{equip_disp}	Fraction of Photoresist from residue in equipment	0.01	(17)
$N_{workers}$	Number of workers exposed to photoresist chemicals	20 to 25 workers/site. See section 3.3.1	(18)
RHO_{photo}	Photoresist density	1 kg/L	Chemical Density Searches (http://www.google.com)

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