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THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

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**EMISSION SCENARIO DOCUMENT (ESD) ON CHEMICAL VAPOUR DEPOSITION IN THE  
SEMICONDUCTOR INDUSTRY**

**Series on Emission Scenario Documents  
No. 35**

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Series on Emission Scenario Documents  
No. 35**

**EMISSION SCENARIO DOCUMENT (ESD) ON CHEMICAL VAPOUR DESPOSITION  
IN THE SEMICONDUCTOR INDUSTRY**

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**INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS**

A cooperative agreement among **FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD**

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## EXPLANATORY NOTES

### **Purpose and background**

This Organisation for Economic Co-operation and Development (OECD) Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns, and potential release pathways of chemicals used as chemical vapour deposition (CVD) precursors in the semiconductor industry. The document presents standard approaches for estimating environmental releases and occupational exposures, and discusses the typical engineering controls used to mitigate exposure to CVD precursors.

This ESD may be periodically 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](mailto:env.riskassessment@oecd.org)). The comments received will be forwarded to the OECD Task Force on 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](http://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 both volatile and nonvolatile chemicals used in CVD. Some 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 U.S. Environmental Protection Agency (EPA) developed this ESD using relevant data<sup>1</sup> and available information on the semiconductor industry, including process description, operating information, chemicals usage, waste generation, waste treatment, worker activities, and exposure information.

The primary sources of information cited in this ESD include the Kirk-Othmer, the Registration, Evaluation and Authorisation of CHEMicals (REACH) guidance, the U.S. Census Bureau's Economic Census, various EPA and other government sources (e.g. CEB, OECD, and

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<sup>1</sup> Please refer to Section 8 for a list of the specific references used in developing this ESD.

regional/state pollution prevention organizations), and data obtained through consultation with industry, including industry trade association surveys. The following industry members provided data and/or input during the development of the ESD:

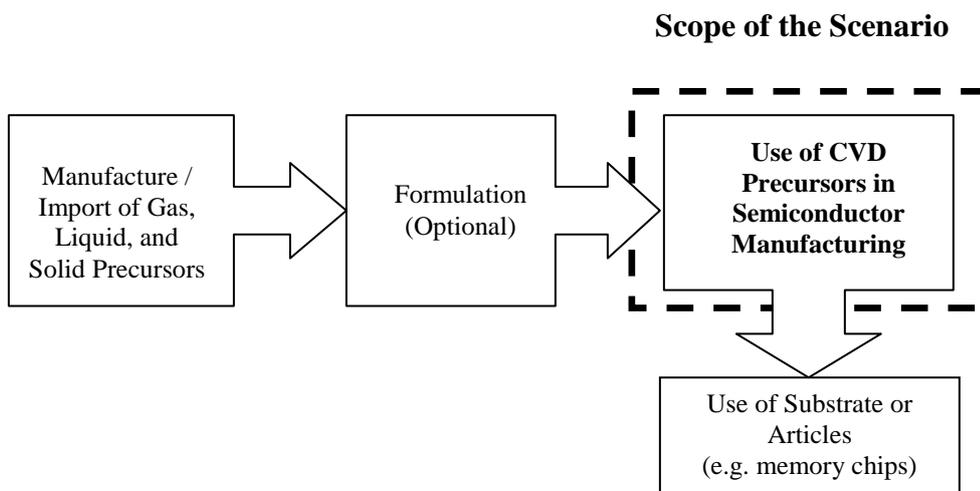
- AIRGARD, Inc.
- Air Liquide Technology
- Air Products & Chemicals, Inc.
- CS Clean Systems AG
- Edwards Limited
- Matheson Tri-Gas
- SEMATECH and its member companies
- Semiconductor Industry Association (SIA) and its member companies

Additional information on the sources investigated and the references cited in this document are presented in Section 8.

The purpose of CVD in semiconductor manufacturing is to deposit layers of thin films on the silicon wafer. The deposited materials either provide desirable properties on portions of the semiconductor or serve as masks for subsequent processing. While CVD precursors may be gases, liquids or solids, this ESD primarily focuses on gaseous and liquid precursors, which are the predominant physical forms. The use of these precursors in semiconductor manufacturing takes place in a fully enclosed process tool within a clean room environment with substantial automation and control. The engineering controls are implemented for two primary purposes: 1) to prevent contamination of highly technical and sensitive semiconductor processes; and 2) to prevent uncontrolled environmental releases and subsequent worker exposures to CVD precursors, many of which are pyrophoric, corrosive and/or harmful to human health.

The ESD covers the end use of CVD precursors in semiconductor manufacturing. The ESD does not cover the manufacture and processing (formulation) of the chemicals prior to end use, although most precursors are expected to be supplied to end users in their neat form without further formulation.

During the development of this ESD, EPA obtained additional information related to container cleaning at the manufacturer (chemical supplier) site, and included this information in Appendix C and D for reference. However, releases and exposures at the manufacturer site are not within the scope of this ESD. An illustration of the scope of this document within the context of the life cycle of the chemical of interest is provided below.



CVD precursors are essentially “chemical intermediates” that react upon deposition. The majority of environmental releases from end use result from the treatment and disposal of unreacted chemicals. The release estimation method presented in this document covers volatile CVD precursors. EPA defines a chemical as volatile if the vapour pressure is at or greater than 0.001 torr at room temperature.

The methods for estimating the following facility operating parameters and the releases are discussed in this ESD:

- Number of sites in the United States involved in semiconductor manufacturing;
- Releases of unreacted precursors from the deposition process (air);
- Number of workers that may be involved in the CVD operation; and
- Potential for worker exposure during CVD operation.

This ESD also discusses the engineering controls, abatement technology, and personal protective equipment employed at semiconductor manufacturing facilities and how they mitigate the potential for release and exposure. Note worker exposure to CVD precursor is expected to be negligible at semiconductor sites.

### **How this document was developed**

The EPA, with support from Eastern Research Group, Inc. (ERG), has developed this ESD on chemical vapour deposition in the semiconductor industry. The scope of the ESD is designed to serve the needs of both EPA and OECD programs. The Risk Assessment Division (RAD) 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), including Premanufacture Notice (PMN) reviews. While OECD ESDs traditionally focus on the potential releases of chemicals from industrial processes, this document also addresses the potential occupational exposures to

chemical precursors used in CVD. Worker exposure information is included so that the ESD may be used to fully support EPA's chemical review programs.

This ESD supersedes EPA's Generic Scenario on *Film Deposition in Integrated Circuit Fabrication* (CEB, 1994). The earlier document has been revised and expanded to meet EPA's revised quality standards for generic scenarios (Chemical Engineering Branch of EPA, 2014).

### **Changes to previous Emission Scenario Document**

This ESD has been revised since the May 2013 version to incorporate comments and data received from industry. Specific changes to the ESD are:

- Discussion of detailed risk management practices and engineering controls utilized at semiconductor manufacturing sites;
- Inclusion of current abatement technology and their destruction and removal efficiency with respect to CVD precursors;
- Revision of release media associated with "Release 1" from air to "air or water" to conservatively account for releases due to abatement inefficiencies;
- Removal of "Release 2" based on industry data indicating that CVD precursors are converted and/or destroyed within abatement technology;
- Enhanced discussion of worker exposure, based on industry data confirming that exposure to CVD precursor is negligible;
- Removal of the previous Appendix B, which contained standard CEB models that are no longer relevant to the ESD;
- Addition of Appendix E to include worker monitoring data at semiconductor manufacturing sites;
- Editorial changes suggested by industry members.

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



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## 1 INDUSTRY SUMMARY AND BACKGROUND

1. In 2011<sup>2</sup>, the US Census Bureau reported 992 companies (USCB, 2011b) under North American Industry Classification System (NAICS) code 334413 for semiconductor manufacturing, employing 55,229 production workers (USCB, 2011a)<sup>3</sup>. The majority of these establishments are geographically concentrated in the state of California, followed by the state of Texas. The Semiconductor Industry Association (SIA) reported worldwide monthly semiconductor sales of 24.70 billion dollars in May 2013, which represents a change of 1.25 percent from a year ago. Sales in the Americas<sup>4</sup> totaled 4.603 billion dollars in May 2013 (SIA, 2013).

2. A semiconductor is a material with electrical characteristics between that of a conductor and an insulator. Semiconductor devices are electronic components used to process and store information in a variety of industrial and consumer products, including computers, electronics, machinery, telecommunication, and transportation equipment. The industry is extremely competitive with cyclical demand and rapid technological changes and advances.

3. Semiconductors are typically created on polycrystalline silicon *wafers*<sup>5</sup> of varying sizes. Depending on the design, a single 300-mm wafer can produce several hundred semiconductor devices or “chips”. Each chip can contain tens of millions of transistor circuits.

4. The semiconductor manufacturing clean room (commonly called the “fab” for fabrication facility) is a unique manufacturing environment. In a typical fab manufacturing semiconductor devices, the temperature, humidity, and particle contamination in the air are tightly controlled. Only 100 particles 1/10,000 of a millimeter or larger in diameter per cubic meter are tolerated. Uncontrolled chemical vapours and gases are equally unacceptable because of their potential to contaminate

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<sup>2</sup> The most recent Census industry data available at this time is 2011.

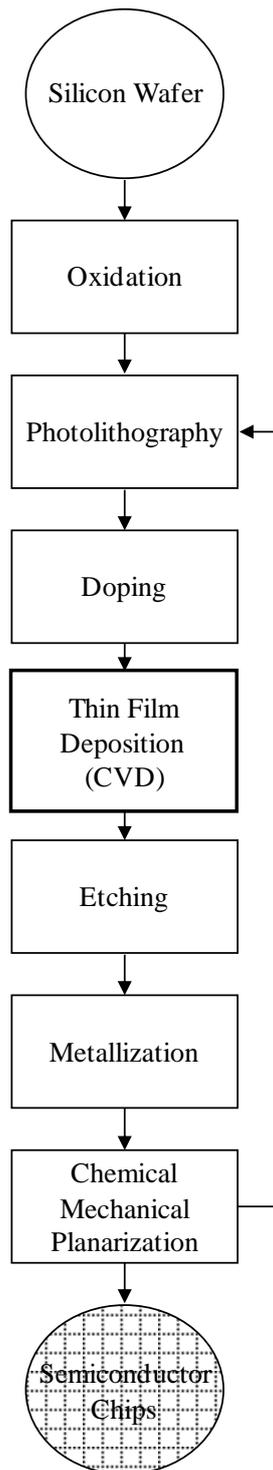
<sup>3</sup> SIA believes U.S. Census Bureau employment and establishment data for the U.S. semiconductor industry is undercounted. The bureau of Labor Statistics (BLS) reported total semiconductor industry employment (NAICS 334413) for 2011 to be 188,358 and total number of establishments to be 1,604 (please refer to BLS website at <http://www.bls.gov/data/>). SIA believes BLS figures are more accurate. In addition, NAICS 334413 does not account for semiconductor industry establishment which are purely dedicated to semiconductor design. SIA considers such establishments and workers as part of the industry. When SIA accounts for these additional employees and adds them to the BLS numbers, SIA estimates current U.S. semiconductor industry employment to be 244,800. For more information on SIA’s employment data, please see SIA’s white paper on the topic at: [http://www.semiconductors.org/clientuploads/Jobs%20Rollout/Jobs%20Issue%20Paper\\_April\\_2013.pdf](http://www.semiconductors.org/clientuploads/Jobs%20Rollout/Jobs%20Issue%20Paper_April_2013.pdf).

<sup>4</sup> SIA data for the Americas presumably include sales for both North and South America.

<sup>5</sup> A *wafer* is a thin disc of semiconductor material, typically from 100 to 300-mm in diameter. It serves as the substrate for the fabrication of integrated circuits. Substrates can be silicon or other semiconductor materials such as gallium arsenide.

wafers; chemical vapour control systems further enhance a safe and healthy working environment.

5. A single semiconductor device is manufactured in layers and can contain billions of transistors. The basic manufacturing process is simple in concept but complex in practice, with hundreds of manufacturing process steps conducted iteratively on as many as 80 different pieces of manufacturing equipment. Depending on the complexity of the design, it takes between 30 to 90 days to transform a wafer into a semiconductor (Berkeley, undated; Shah, 2008). The process steps also vary from company to company. The exact technical design is highly confidential and is continually evolving. The OECD Environment, Health and Safety Publications Series on Emission Scenario Documents No. 9: *Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing* (OECD, 2010) provides information on the semiconductor industry and the general processes within this industry. Semiconductor manufacturing processes include oxidation, photolithography, doping, thin film deposition – such as chemical vapour deposition (CVD) or physical vapour deposition (PVD), etching, metallization, and chemical mechanical planarization (CMP). Figure 1-1 illustrates the basic process steps. The following sections describe the main processes in semiconductor manufacturing, including film deposition, which is the focus of this ESD.



**Figure 1-1. Overall Process Flow Diagram – Semiconductor Manufacturing<sup>6</sup>**  
(OECD, 2010)

<sup>6</sup> Wafers undergo multiple iterations of the steps from photolithography to CMP, as indicated by the return arrow.

## 1.1 Photolithography

6. Photolithography is used in semiconductor manufacturing to form a surface pattern on the wafer. This is done using a light-sensitive, organic solvent-based material called photoresist. An adhesion promoter is first applied to the wafer to improve the adherence and uniformity of the resist coating. Then, a fixed amount of photoresist is dispensed onto the wafer surface using a high speed rotating element. An edge bead removal (EBR) step is commonly performed to remove any beads of photoresist on the edge of the wafer.

7. The wafer is soft baked to remove most of the carrier solvent, and exposed to specific wavelengths of light, lasers, electron beams, or other means to introduce a pattern to the wafer surface. This may be done through the use of a template mask, which is a glass plate containing an image of the desired circuit.

8. Finally, a photoresist developer is applied to remove unwanted portions of the resist, or to create a “patterned” wafer for further processing. The number of photolithography steps during manufacturing increases as the complexity of the design increases.

9. Examples of chemicals used in photoresist coatings include photoreactive monomers and solvents such as propylene glycol monomethyl ether acetate (PGMEA) and ethyl lactate. Photoresists used in the manufacturing process are ultimately removed from the wafer. Additional information on the different types of chemicals used in photoresist applications and the associated environmental releases can be found in OECD Environment, Health and Safety Publications Series on Emission Scenario Documents No. 9: *Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing* (OECD, 2010).

## 1.2 Film Deposition and Metallization

10. In film deposition, layers of single crystal silicon, polysilicon, silicon nitride, silicon dioxide, or other materials are deposited onto the wafer either to provide desirable properties on portions of the device or to serve as masks. Thin film deposition techniques are also used in metallization to provide interconnects for electrical devices during the final stages of manufacturing. The deposited film layer is a few micrometers thick on the wafer surface. Thin film formation techniques include physical vapour deposition (PVD), chemical vapour deposition (CVD), and thin film formation from a chemical solution.

11. In PVD, atoms are vapourized from a source, transported to a substrate, and condensed onto the substrate to form a coating. The deposited film usually consists of the same type of material as the source, making PVD essentially an evaporative process.

12. In CVD, one or more precursor chemicals are vapourized from a source, transported into a flow reactor, and reacted to form a nonvolatile layer of solid film on the substrate. Both PVD and CVD occur in a closed, controlled environment (Kirk-Othmer, 2003). The CVD process is discussed in further detail in Section 2.

13. Films may also be deposited using a chemical solution. Electroplating, the process of depositing metallic ions in an electrolysis cell, is a technique of this type used in the semiconductor industry. Electroplating usually takes place in a tank of solution containing negatively charged metal ions. Metal deposition occurs when the ions move toward the positively charged substrate to form a layer of metal coating. Most electroplating systems use an inorganic metal salt with an acid bath. A common example in the semiconductor industry is the electroplating of copper using copper sulfate ( $\text{CuSO}_4$ ) to form interconnects for electrical devices (Kirk-Othmer, 2004).

### **1.3 Etching**

14. Etching is used in semiconductor manufacturing to chemically remove specific areas of the deposited film so that an underlying material is exposed or another material may be deposited in place of the etched material. Etching is typically done after the application of a photoresist. Etching may be performed in a wet process using solutions of acids, bases or oxidizers, or in a dry process using various gases excited by striking a plasma. The dry etch process provides more precision and is commonly used in electronic devices with smaller features (EPA, 1999).

15. Some common chemicals used in wet etch include hydrofluoric acid, phosphoric acid, nitric acid and acetic acid. Dry etching typically utilizes halogenated gases (EPA, 1999).

### **1.4 Chemical Mechanical Planarization (CMP)**

16. The purpose of chemical mechanical planarization (CMP) is to planarize the surface material on the wafer to provide an even topography for subsequent processing. CMP typically follows a film deposition step. The planarization process is performed through the use of a mechanical polisher with one or more chemical slurries. The slurry contains abrasive particles that serve to mechanically remove the film layer, as well as a chemical solvent or surfactant that serves to either selectively react with or protect a film material during polishing. Silica, alumina, and ceria particles are commonly used as abrasives in the slurry, while potassium hydroxide, ferric nitrate, hydrogen peroxide, and organic compounds are common chemical components in the slurry (EPA, 1999).

## 2 CHEMICAL VAPOUR DEPOSITION PROCESS DESCRIPTION

17. Chemical vapour deposition (CVD) is a chemical process that produces high-purity thin films. In this process, one or more volatile precursors react to deposit the desirable film (e.g. oxide, nitride, silicon, metal layers) onto the substrate. The deposited film serves to provide certain qualities for the semiconductor device or as a mask for subsequent processing.

18. Although CVD precursor may be in the form of a gas, liquid or solid, gas and liquid are the most common physical forms. During deposition, the precursor is vapourized and introduced into a flow reactor, sometimes via a carrier gas (e.g. helium, argon, nitrogen or oxygen), and is broken down through chemical reaction or thermal decomposition. The reaction results in the formation of a nonvolatile layer of solid film on the substrate. In some cases, the deposited material may react with gaseous species to form compounds such as oxides, nitrides, carbides, and borides. The operating temperature is typically 400°C for interconnect dielectrics and refractory metals. In many cases, a vacuum system is attached to the reactor to maintain a suitable deposition pressure (Kirk-Othmer, 2003).

19. Most CVD systems include a mass flow controller, a substrate holder, a reaction chamber, a heat source, and a vacuum pump. These common components serve the following purposes:

- Mass flow controller – to control and deliver the precursor or reactant gases into the reactor;
- Substrate holder – to hold the substrate in place during deposition;
- Reaction chamber – a stainless steel, glass-Pyrex, quartz chamber or tube in which the reaction takes place;
- Heating system with temperature control – to supply heat to the reactor and substrate; and
- Vacuum Pump – to maintain the system pressure and to remove reaction by-products and depleted gases (Kirk-Othmer, 2006).

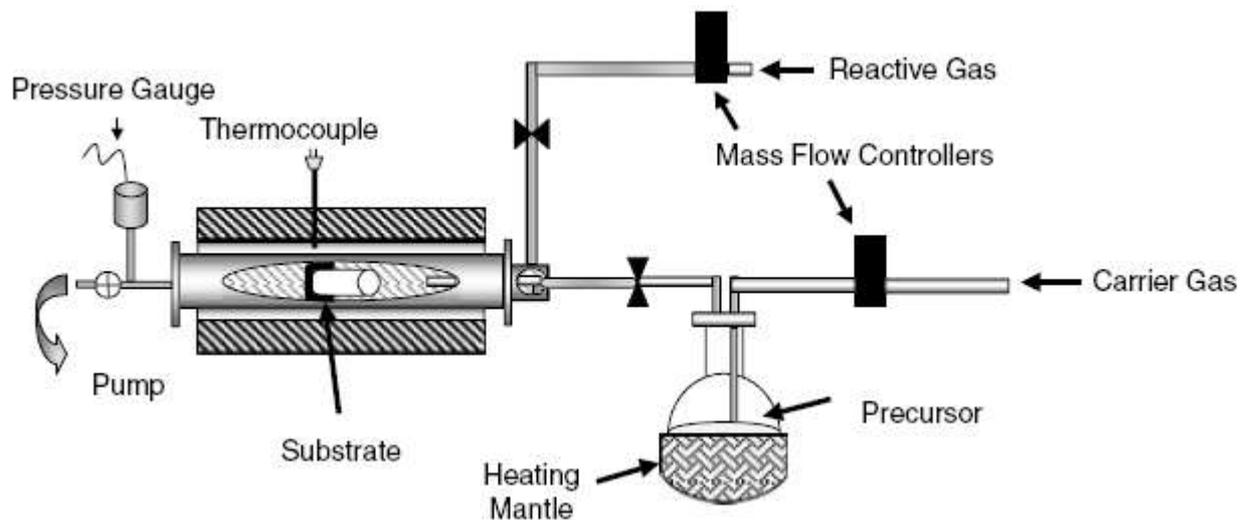
20. Examples of different CVD techniques include: thermally activated CVD, low pressure CVD of polysilicon, metalorganic CVD (MOCVD) of epitaxial layers, plasma-enhanced CVD (PECVD), and atomic layer deposition (ALD). The remainder of this section describes some of the various types of CVD processes and the common materials used in the industry.

## 2.1 Thermally Activated Chemical Vapour Deposition

21. Thermal CVD is a process initiated only using thermal energy. The process is typically conducted under vacuum and uses either a hot- or a cold-wall reactor. In a hot-wall reactor, a large volume of processing gases and substrates are heated using an external heat source outside the reactor. In a cold-wall reactor, gases are heated locally through inductive heating of the substrate or the substrate fixture. Thermal CVD processes are used extensively to grow high quality epitaxial thin films (e.g. epitaxial silicon films) and metal films (Kirk-Othmer, 2006).

## 2.2 Metalorganic Chemical Vapour Deposition (MOCVD)

22. MOCVD is a subset of thermal CVD processes using metalorganic gases or liquids as the source. An example of a metalorganic compound, an organic compound containing a metal atom, is Tetrakis(dimethylamino)titanium (TDMAT). The greatest advantage of using metalorganic precursors is that they are volatile at relatively low temperatures and can therefore be easily transferred to the substrate. The flow rate and partial pressures of the gases can be precisely controlled, allowing for efficient and reproducible deposition. Figure 2-1 provides a schematic of a typical metalorganic CVD system (Kirk-Othmer, 2006).



**Figure 2-1. General Diagram of Equipment Used in Metalorganic Chemical Vapour Deposition**

Source: Kirk-Othmer, 2006.

## 2.3 Plasma-Enhanced Chemical Vapour Deposition (PECVD)

23. In PECVD, the deposition is enhanced by striking a plasma in the reaction chamber to overcome kinetic barriers, allowing for rapid deposition at lower temperatures. The plasmas are generated by DC, RF, or electrocyclotron resonance (ECR) techniques. The reactor can be coupled either inductively with a coil or capacitively with electrode plates forming plasma. This type of CVD reactor is commonly used to deposit films such as silicon nitride or  $\text{Si}_3\text{N}_4$ .

## 2.4 Types of CVD Precursor Chemicals

24. Chemicals are used in CVD processes as precursors for deposition, as carrier gases, and as cleaning agents to remove reaction byproducts in the chamber. Table 2-1 lists some common examples of semiconductor CVD precursors – the chemicals of interest in this ESD. Carrier gases (e.g. argon, helium, nitrogen or hydrogen), which are usually inert, and cleaning chemicals (e.g. nitrogen trifluoride, perfluorocarbons, etc) are outside the scope of this document.

**Table 2-1: Some Common Precursors and Corresponding Thin Films Grown by Chemical Vapour Deposition**

Precursor	Physical Form at 25°C and 1 atm	Thin Films by CVD
Silane (SiH <sub>4</sub> )	Gas	Si and Si containing materials
Ammonia(NH <sub>3</sub> )	Gas	Nitrides
Phosphine (PH <sub>3</sub> )	Gas	Phosphides
Silicon Tetrachloride (SiCl <sub>4</sub> )	Liquid	Si and Si containing materials
Trimethylsilane (CH <sub>3</sub> ) <sub>3</sub> SiH	Gas	Si and organosilicate glass low-k precursor
Germanium Tetrachloride (GeCl <sub>4</sub> )	Liquid	Ge and Ge containing films
Titanium Tetrachloride (TiCl <sub>4</sub> )	Liquid	TiN and Ti containing films
Pentakis(dimethylamino) tantalum (PDMAT)	Solid	TaN and Ta containing films
Tetrakis[DiEthylAmino] hafnium Hf[N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>4</sub>	Liquid	HfO and Hf containing materials
Tungsten Hexafluoride (WF <sub>6</sub> )	Gas	W and W containing materials
Trimethyl aluminum Al <sub>2</sub> (CH <sub>3</sub> ) <sub>6</sub>	Liquid	Al and Al containing materials
Dichlorosilane (SiH <sub>2</sub> Cl <sub>2</sub> )	Gas	Silicon dioxide, epitaxial and polycrystalline silicon
Trichlorosilane (HSiCl <sub>3</sub> )	Liquid	Epitaxial silicon
Tetraethylorthosilicate, TEOS (Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> )	Liquid	Silicon dioxide
Trimethyl borate (B(OCH <sub>3</sub> ) <sub>3</sub> )	Liquid	Borosilicate glass
Tetrakis(dimethylamido)titanium (Ti(NMe <sub>2</sub> ) <sub>4</sub> )	Liquid	Titanium nitride and carbonitride

Source: Kirk-Othmer, 2006; Praxair, 2010; Air Products, 2013; Matheson, 2013; Sigma-Aldrich, 2013.

## 2.5 CVD Safety in Semiconductor Manufacturing

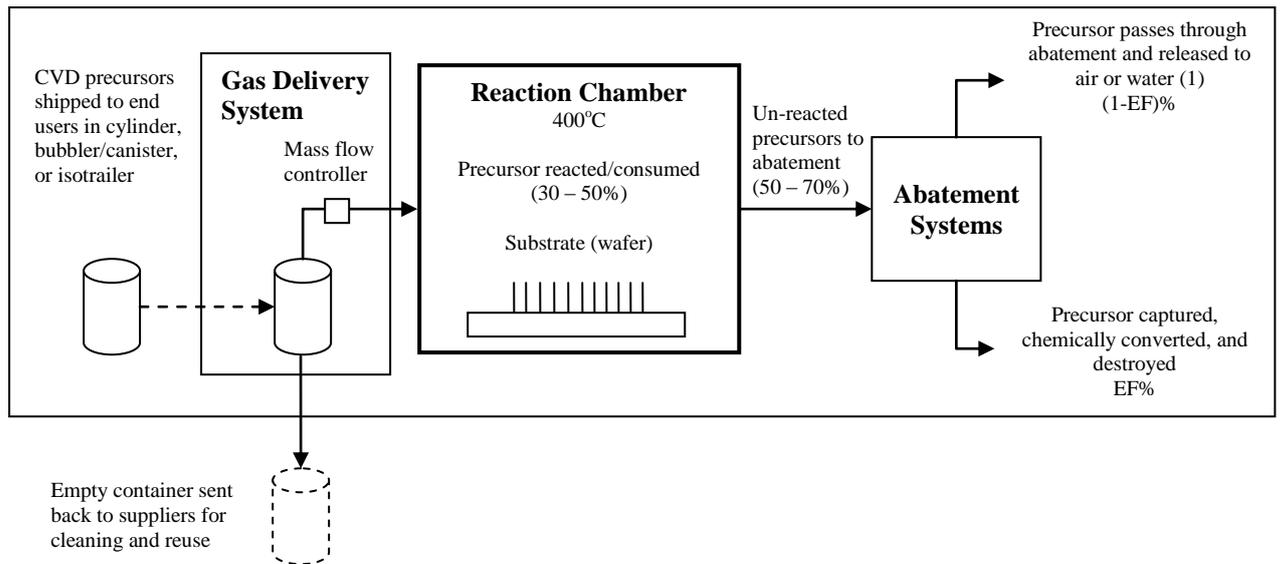
25. The semiconductor industry employs risk management measures (RMM) to protect workers and the environment. The RMMs, which often exceed regulatory requirements, are the result of numerous guidelines developed through Semiconductor Equipment and Materials International (SEMI) and collaboration between suppliers of process tools, suppliers of chemicals, and semiconductor manufacturers.

26. RMMs such as chemical assessments, selection and control procedures, hazardous gas management systems, segregated exhaust systems, safety interlocks, and spill control/prevention – are common in semiconductor fabs. New fabs use totally enclosed processes, automation, and chemical delivery systems to create a barrier between workers and the process and to protect against chemical and physical hazards in the work environment. In many cases, secondary and even tertiary redundancy to these controls ensures that the necessary protection will be provided if one control fails. Because of the considerable control measures within a state-of-the-art semiconductor fab, under normal operating conditions, workers are not exposed to chemical or physical hazards. Numerous voluntary guidelines developed by the industry promote manufacturing equipment designs that minimize risk to workers whether during normal operation or during maintenance procedures. In addition to the safety systems such as interlocks and automated purge systems that protect workers during maintenance when normal risk management measures may have to be bypassed, workers use personal protective equipment (PPE) when needed to ensure their safety.

27. Gas cabinets for enclosing and exhausting potentially hazardous leaks from gas cylinders are specifically designed by, and used for, the semiconductor industry. These gas cabinets include safety features appropriate for the application, including steel construction, self-closing doors, negative ventilation, automatic fire sprinkler systems, excess flow sensors, gas leak monitoring, and automatic shut-off (Industry, 2009).

28. CVD processes are conducted inside an enclosed process chamber. Precursor substances, many of which are toxic or flammable (e.g. silane is pyrophoric), are delivered to the deposition chamber through appropriate hazardous gas management systems and safety interlocks. During deposition, precursors are essentially intermediates that react to form another substance. Any unreacted precursor is removed by the process chamber exhaust systems; the systems are typically segregated to ensure proper handling and treatment and to prevent reactions between incompatible substances (e.g. acids, bases, solvents). Process chamber exhaust is routed to various abatement systems, in which the precursors are chemically converted and destroyed (SEMATECH, 2007).

29. Worker exposure to CVD precursors is not expected during semiconductor manufacturing, although there is potential for exposure to degradation products during maintenance activities. Figure 2-2 summarizes typical release and exposure points from a CVD operation. Note this ESD does not attempt to assess exposures to degradation products.



Environmental Releases:

1. Unreacted gas passed through abatement (release to air or water)

Occupational Exposure:

Exposure to precursor is expected to be negligible.

Note: Environmental release and worker exposure related to container cleaning occurs at supplier's site (not within the scope of this document). Additionally, this ESD does not assess the potential for exposure to degradation products during equipment maintenance.

**Figure 2-2. Typical Release and Exposure Points during Chemical Vapour Deposition**

### 3 OVERALL APPROACH AND GENERAL FACILITY ESTIMATES

30. This ESD presents EPA's standard approach for estimating environmental releases of CVD precursors during semiconductor fabrication. Although there are several types of CVD processes, their associated release and exposure points are expected to be the same.

31. The estimation methods described in this document utilize available industry-specific information and data to the greatest extent possible. It should be noted the default values cited throughout this document are intended to be used only when appropriate site-specific or chemical-specific information is not available.

32. This section of the ESD presents general facility calculations for the semiconductor industry, which include estimates of the daily use rates of CVD precursors, the number of semiconductor manufacturing sites using the chemicals of interest, and the number of operating days at these sites.

33. Section 4 of the ESD presents environmental release assessments from the use of precursors in CVD processes. This section utilizes the general facility estimates to determine the quantity of chemical released from various points in the wafer fabrication process and the most likely media of release for each source.

34. Section 5 of the ESD qualitatively discusses exposures during semiconductor manufacturing. Exposure during CVD is expected to be negligible due to the use of engineering controls and personal protective equipment (PPE).

#### 3.1 Introduction to the General Facility Estimates

35. Through the remainder of this section, EPA utilizes available industry and U.S. Census data to estimate the number of semiconductor manufacturing sites in the U.S. Because CVD is a crucial process in wafer fabrication, all semiconductor sites are expected to engage in CVD operations. Therefore, some general facility estimates presented in the OECD Environment, Health and Safety Publications Series on Emission Scenario Document No. 9: *Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing*, are applicable to this document. This section also describes the methods used and the assumptions made to estimate the typical use rate for a CVD precursor and the number of transport containers used annually to transfer a potential chemical of interest.

36. In this ESD, an *end user* of the chemical of interest (CVD precursor) is defined as a semiconductor manufacturing facility. Table 3-1 summarizes the general facility estimates and the ESD section in which they are discussed.

**Table 3-1: Summary of General Facility Parameters**

<b>Parameter</b>	<b>Description</b>	<b>ESD Section</b>
$TIME_{operating\_days}$	Number of operating days at a semiconductor manufacturing facility (days/yr)	3.2
$F_{chem}$	Concentration of CVD precursor as received at semiconductor manufacturing facilities (kg chemical/kg formulation)	3.3
$Q_{chem\_yr}$	Annual use rate of CVD precursor (kg/yr)	3.4
$Q_{chem\_site\_day}$	Daily use rate of CVD precursor (kg/site-day)	3.5
$N_{sites}$	Number of sites using the CVD precursor (sites)	3.6
$N_{container\_unload\_site\_yr}$	Number of transport containers unloaded at each site per year (containers/site-yr)	3.7

### 3.2 Days of Operation ( $TIME_{operating\_days}$ )

37. The Semiconductor Industry Association (SIA) provides the following estimates on the annual number of operating days for semiconductor fabrication: 250 (low-end) to 360 days (high-end) for a large scale operation and 250 days for a small scale, niche<sup>7</sup> operation (SIA, 2003). If specific information is not available to estimate the days of operation ( $TIME_{operating\_days}$ ) at a semiconductor manufacturing site, a default value of 360 days per year should be assumed. This value is consistent with the default value described in the OECD Environment, Health and Safety Publications on Emission Scenario Documents No. 9: *ESD on Photoresist Use in Semiconductor Manufacturing*. CVD process is expected to take place every day during which the site is in operation.

### 3.3 Physical Form and Concentration of the CVD Precursor ( $F_{chem}$ )

38. CVD precursors may be supplied as a solid, liquid, or gas. Solid precursors with a low melting point may be heated and swept with an inert carrier gas for deposition while those with a high melting point may be heated and sublimed. Liquid precursors may be vapourized at the point of use and gaseous precursors are used directly. This ESD assumes the chemical of interest would either be a gas or a liquid because these are the predominant physical forms for CVD precursors (Industry, 2009-2010).

39. While some precursors can be supplied in a formulation – for example, some chemicals may be dissolved in an inert solvent – most precursors are supplied to the end users (semiconductor manufacturing sites) as pure substances. These precursors are expected to be more than 99.99% pure. For the purpose of the assessment, the concentration of the precursor ( $F_{chem}$ ) is assumed to be 100% as default.

<sup>7</sup> 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).

### 3.4 Annual Use Rate of CVD Precursor ( $Q_{\text{chem\_yr}}$ )

40. The precursor use rate is highly process-dependent and is directly associated with the production volume. Such data are considered proprietary information in the semiconductor industry and therefore are not widely available. In lieu of such data, the high-end annual use rate of a single CVD precursor ( $Q_{\text{chem\_yr}}$ ) can be estimated using the production volume of the chemical, which is readily available in the Pre-Manufacture Notices (PMNs) submitted to EPA. The production volume represents the maximum quantity of chemical available to all end users.

### 3.5 Daily Use Rate of CVD Precursor ( $Q_{\text{chem\_site\_day}}$ )

41. As discussed previously, the daily use rate of a precursor depends on the process and scale of production at the end use facility. One U.S. specialty chemical supplier suggests that the annual site-specific use rate ( $Q_{\text{chem\_site\_yr}}$ ) for a single precursor can vary from 25 to 1,000 kilogram per year (Industry, 2009). Based on this information, the high-end and low-end site-specific daily use rate of a CVD precursor can be estimated using the following equation:

$$Q_{\text{chem\_site\_day}} = \frac{Q_{\text{chem\_site\_yr}}}{\text{TIME}_{\text{operating\_days}}} \quad (3-1)$$

Where:

$Q_{\text{chem\_site\_day}}$	= Daily use rate of CVD precursor (kg/site-day)
$Q_{\text{chem\_site\_yr}}$	= Annual use rate of CVD precursor (Range: 25 to 1,000 kg/site-yr; Default value: 1,000 kg/site-yr)
$\text{TIME}_{\text{operating\_day}}$	= Number of operating days at semiconductor manufacturing site (Default: 360 days/yr)

42. This ESD provides methods to estimate both low-end and high-end use rates. If the CVD operation occurs in a larger-scale production facility, the high-end value (1,000 kg/site-yr) should be used to provide conservative estimates. A search of recent Pre-Manufacture Notice (PMN) submissions indicates that the use rate generally ranges from 50 to 1,000 kg/site-yr<sup>8</sup>, which is consistent with the default range recommended in the ESD. Because this parameter is highly process dependent, estimates for the daily use rate of a CVD precursor should always be made on a case-specific basis when possible. When information is not readily available, engineering judgment should be applied when estimating the chemical use rate.

### 3.6 Number of Sites ( $N_{\text{sites}}$ )

43. The number of facilities using the chemical of interest ( $N_{\text{sites}}$ ) depends on the total annual production of the chemical of interest ( $Q_{\text{chem\_yr}}$ ) (minus the amount lost (e.g. not used in the process) as residual in empty containers ( $F_{\text{container\_disp}}$ )), the daily

<sup>8</sup> Based on a search of the PMN database, there were 8 relevant PMN submissions from January 2007 to September 2010. The chemical use rate was estimated to be 50 – 1,000 kg/site-yr in 7 cases; the use rate exceeded 1,000 kg/site-yr in one case.

use rate of the chemical of interest ( $Q_{\text{chem\_site\_day}}$ ), and the annual operating days ( $\text{TIME}_{\text{operating\_days}}$ ). Equation 3-2 demonstrates how the number of semiconductor manufacturing facilities using a chemical of interest could be determined.

$$N_{\text{sites}} = \frac{Q_{\text{chem\_yr}} \times (1 - F_{\text{container\_disp}})}{Q_{\text{chem\_site\_day}} \times \text{TIME}_{\text{operating\_days}}} \quad (3-2)$$

Where:

$N_{\text{sites}}^9$	=	Number of sites using the precursor chemical (sites)
$Q_{\text{chem\_yr}}$	=	Annual production volume of precursor chemical (kg chemical/yr for this use)
$Q_{\text{chem\_site\_day}}$	=	Daily use rate of CVD precursor (kg chemical/site-day)
$F_{\text{container\_disp}}$	=	Fraction of chemical remaining in the transport container (Default: 0.1 kg residual chemical / kg chemical in container based on ISMI survey results in Table D-1)
$\text{TIME}_{\text{operating\_days}}$	=	Number of operating days at semiconductor manufacturing sites (days/yr) (Default: 360 days/yr)

44. The default value for  $F_{\text{container\_disp}}$  is based on an ISMI survey of CVD precursor suppliers.

45. Note that the calculated value of  $N_{\text{sites}}$  should not exceed the total number of semiconductor manufacturing facilities known to operate in the United States. The Economic Census estimated a total of 922 semiconductor manufacturing facilities in the United States in 2011 (see Table 3-2).

**Table 3-2. 2011 Census Data on the Number of U.S. Facilities for the Semiconductor and Related Device Manufacturing Industry Sector (NAICS 334413)**

Employment-Size Class	1-19	20-99	>100	Total
Number of Facilities	547	199	176	922
(% of total)	(59%)	(22%)	(19%)	(100%)

Source: USCB, 2011b. Refer to USCB, 2011b in Section 8 for more detailed facility size and employee distribution information.

<sup>9</sup>The value for  $N_{\text{sites}}$ , calculated using Equation 3-2 should be rounded up to the nearest integer value.  $Q_{\text{chem\_site\_day}}$  should then be adjusted for the  $N_{\text{sites}}$  integer value (to avoid errors due to rounding):

$$Q_{\text{chem\_site\_day}} = \frac{Q_{\text{chem\_yr}}}{N_{\text{sites}} \times \text{TIME}_{\text{operating\_days}}}$$

Note: If the number of sites is known, the previous equation may also be used to estimate the resulting average annual production rate for use in subsequent calculations.

### Summary of the Relationship of General Facility Parameters

The values for days of operation ( $TIME_{operating\_days}$ ), daily use rate of the chemical of interest ( $Q_{chem\_site\_day}$ ), and number of manufacturing sites ( $N_{sites}$ ) are related. This ESD presents one method for estimating  $N_{sites}$  using estimated default values for: 1) the annual production quantity of a precursor; 2) the total number of operating days per year at the end use site; 3) the mass fraction of the precursor remaining as residue in the transport container; and 4) the daily use rate of a precursor at a single site.

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

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

If  $N_{sites}$  is known and  $TIME_{operating\_days}$  is unknown, EPA recommends that using the default assumption that CVD operations occur 360 days per year and  $Q_{chem\_site\_day}$  be calculated using the above equation.

EPA recommends calculating the chemical of interest throughput based on the methodology presented in Section 3.5, and compare it to the throughput based on number of sites and operating days, as calculated above.

### 3.7 Number of Transport Containers Unloaded per Site ( $N_{container\_unload\_site\_yr}$ )

46. CVD precursors are commonly supplied in stainless steel, carbon steel, aluminum, or electroless nickel coated carbon steel containers (Air Liquide, 2010). Typical containers used in semiconductor manufacturing are 16 gallons in size (Shah, 2010), although smaller containers are also used (Industry, 2009-2010)<sup>10</sup>. See Table C-1 for the typical range of container sizes and styles. The number of transport containers unloaded annually per site can be estimated based on the daily use rate, container size, and the purity of the precursor. Gaseous precursors are packaged as compressed gases or pressurized liquids. Therefore, the density of these substances differs from that at atmospheric conditions.

$$N_{container\_unload\_site\_yr} = \frac{Q_{chem\_site\_yr}}{F_{chem} \times V_{container} \times \rho_{formulation}} \quad (3-3)$$

Where:

$N_{container\_unload\_site\_yr}$  = Number of transport containers unloaded at each site per year (containers/site-yr)  
 $Q_{chem\_site\_yr}$  = Annual use rate of CVD precursor (Default value: 1,000 kg/site-yr)

<sup>10</sup> One specialty chemical supplier indicated the use of ampoules of 1L to 30L in size (approximately 0.3 – 8 gallon; Industry, 2009).

$F_{\text{chem}}$	=	Weight fraction of precursor in the formulation as received (Default: 1 kg chemical/kg formulation)
$V_{\text{container}}$	=	Volume of transport container (Default: 16 gallon or 60.6 L container)
$\rho_{\text{formulation}}$	=	Density of chemical formulation (kg/L formulation; Default: 1 kg/L for liquid and 0.52 kg/L for gaseous precursor in pressurized container. The default value assumes the gas would be pressurized and packaged as a liquid. <sup>11</sup> )

47. For reasons of cleanliness and toxicity, CVD precursor containers are not cleaned at semiconductor manufacturing sites (Shah, 2008). Empty containers are typically shipped back to the supplier for reuse.

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<sup>11</sup> Default values based on the density of trimethyl silane shipped in pressurized containers (Air Products, 2006). At this density, the gaseous precursor is expected to be a liquid. See Appendix C for alternate values.

#### 4 ENVIRONMENTAL RELEASE ASSESSMENTS

48. This section presents an approach to quantify the amount of precursor substance released during CVD processes. Table 4-1 presents the release source, the likely media of release, and the model used to estimate the release. Where release is expected to be negligible, a qualitative discussion is provided. This ESD assumes the precursor is either a liquid or a gas as they are the predominant physical forms for chemicals used for deposition (Industry, 2009-2010).

**Table 4-1. Summary of Environmental Releases and Likely Media of Release**

Release	Description	Model(s)	Standard EPA Model (✓)	On- or Off-Site Release
1	Process residue – unreacted precursor released to air or water	Loss rate is based on available industry-specific data.		On-site

On-site release – the release occurs at the semiconductor manufacturing site.

49. All release equations below estimate daily release rates for a given site. To estimate annual releases for all sites for a given source, the daily release rates must be multiplied by the number of days of release<sup>12</sup> and by the total number of sites using the CVD precursor ( $N_{\text{sites}}$ ).

50. CVD precursors are essentially “reactive intermediates”, i.e. they react to form another substance for deposition. Unreacted precursors from deposition are routed from the chamber exhaust to abatement, most of which are at least 99 percent efficient. Therefore, only a small fraction of unreacted precursor could ultimately be released to the environment.

51. The entire CVD process from gas delivery to deposition occurs in a closed system where no leakage is expected. Therefore, release from volatilization during these process steps would not occur. Further, release from chamber cleaning is not expected because no CVD precursor is present at this point. Chambers are cleaned in between batches using a plasma etch process to remove residue deposited on the surfaces on the chamber (Semiconductor International, 2009). Cleaning is done remotely using an automated system that introduces atomic fluorine converted from a fluorine-containing gas into the chamber (ISMI, 2005; MICRO, 2005). This ESD does

<sup>12</sup> The number of days of release varies by release activity. In most cases, the number days of release at the semiconductor site equals  $\text{TIME}_{\text{operating\_days}}$ .

not attempt to assess release of degradation products and/or deposition byproducts as the exact chemical released and the associated release quantity depend on the process chemistry, control technology, and the selection of cleaning material.

52. Release from CVD container cleaning operations occurs at the supplier site, and is separately addressed in Appendix D (not within the scope of this ESD). The precursors are not expected to be released directly to the environment because of their hazard and reactivity. The efficiency of the control technology used during cleaning operations to break down these chemicals should be considered when evaluating environmental releases.

#### **4.1 Control Technologies**

53. CVD processes take place in a highly controlled environment. Due to concerns for product contamination and worker safety, chemical delivery systems with safety locks are employed to prevent release of chemicals during transfer operations. Abatement systems are used to treat unreacted gases, including CVD precursors, prior to being released to the environment. Direct environmental releases of CVD precursors are prevented because many of these chemicals react upon exposure to the atmosphere (i.e. direct release of certain chemicals may result in fire or explosion).

54. Process gases from the deposition chamber are treated in point-of-use (POU) abatement system(s) followed by a central house control technology. POU abatements could include burn boxes, wet scrubbing systems, oxidation systems, cold bed systems (adsorber/chemisorber), hot chemical bed systems, and reactor systems. Based on a survey of SIA/ISMI member companies, the common approach is to use a hybrid system that combines both a thermal and a wet component. In the hybrid abatement system, exhaust gases pass through a combustor, where the gases (including CVD precursors) are converted into a combination of soluble materials, particulates, and gaseous byproducts. Following the combustor, the gases are cooled and then scrubbed for further conversion. The scrubbed gases exit the system as exhaust. Any particulates and byproducts from the POU could be further treated and neutralized at the facility's wastewater treatment system.

55. POU controls are typically interlocked with the process equipment (i.e. when the POU control systems fail, the process equipment is shut down). POU controls serve the following purposes:

- Ensure worker health and safety: POU controls abate the potential build-up of flammable and pyrophoric gases used for deposition that can cause a fire and/or explosion in the ductwork, resulting in equipment damage and personnel injury. These gases are also more likely to migrate/leak outside of the ductwork if not immediately treated near the equipment outlet;
- Reduce air emissions: POU controls can provide higher removal efficiency for the compound of interest than the centralized (“end-of-pipe”) scrubbers, thereby reducing environmental releases (SEMATECH, 1997); and
- Reduce production downtime: POU controls prevent solid build-up in the exhaust ductwork. Build-up may be caused by reaction between exhaust

gases, solids from the process, or condensation of vapours. These controls also prevent duct corrosion in cases where corrosive gases are used in semiconductor equipment.

56. Table 4-2 presents some information on the removal efficiencies of common controls based on a 1997 supplier POU control system survey conducted by SEMATECH (SEMATECH, 1997). The data, consistent with more recent information provided by SIA/ISMI, indicate the control efficiency is often 99 percent or higher depending on the process and type of control technology chosen. The efficiency of the control technology should be considered when conducting an environmental release assessment.

**Table 4-2. Compound Removal Efficiencies**

<b>Application / Process</b>	<b>Control Technology</b>	<b>Compound</b>	<b>Percent Removal Efficiency</b>
Silicon EPI with dopants (hydrogen vented)  Gases fed: hydrogen, dichlorosilane or trichlorosilane, dopants, hydrogen chloride	Wet scrubbing (without chemical addition)	Diborane	>98%
		Dichlorosilane	>99.9%
		Hydrogen	0%
		Hydrogen chloride	>99.99%
		Phosphine	0 – 96%*
Silicon EPI with dopants (hydrogen abated)  Gases fed: hydrogen, dichlorosilane or trichlorosilane, dopants, hydrogen chloride	Oxidation with hydrogen present/wet scrubbing	Diborane	>99%
		Dichlorosilane	>99.9%
		Hydrogen	>99.99%
		Hydrogen chloride	>99.99%
		Phosphine	>99%
		Oxides of nitrogen	Not detected
Poly deposition, non-PFC clean  Gases fed: silane (deposition), chlorine trifluoride (chamber clean)	Cold bed	Chlorine trifluoride	>99%
		Hydrogen chloride	>99%
		Hydrogen fluoride	>99%
		Silane	>99%
		Silicon tetrachloride	>99%
		Silicon tetrafluoride	>99%
	Oxidation using electric/wet scrubbing	Chlorine trifluoride	>99%
		Hydrogen chloride	>99%
		Hydrogen fluoride	>99%
		Silane	>99.9%
		Silicon tetrachloride	>99%
		Silicon tetrafluoride	>99%
	Oxidation using fuel (for dep. only); cold bed (for clean	Chlorine trifluoride	>99%
		Hydrogen chloride	>99%
		Hydrogen fluoride	>99%

**Table 4-2. Compound Removal Efficiencies**

Application / Process	Control Technology	Compound	Percent Removal Efficiency
	only)	Silane	>99%
		Silicon tetrachloride	>99%
		Silicon tetrafluoride	>99%
	Oxidation using fuel/wet scrubbing	Chlorine trifluoride	>99.9%
		Hydrogen chloride	>99%
		Hydrogen fluoride	>99%
		Silane	>99.9%
		Silicon tetrachloride	>99%
		Silicon tetrafluoride	>99%
		Carbon monoxide	<1 lb/yr created
	Pre-pump reactor	Oxides of nitrogen	<3 lb/yr created
		Chlorine trifluoride	0%
		Hydrogen chloride	0%
		Hydrogen fluoride	0%
		Silane	>99%
		Silicon tetrachloride	0%
	Wet scrubbing (with chemical addition)	Silicon tetrafluoride	0%
		Chlorine trifluoride	>99%
		Hydrogen chloride	>99%
		Hydrogen fluoride	>99%
		Silane	>80%
Silicon tetrachloride		>99%	
Doped poly deposition Gases fed: silane, phosphine	Cold bed	Silicon tetrafluoride	>99%
		Hydrogen fluoride	>99%
		Phosphine	>99%
		Silane	>99%
	Oxidation using electric/wet scrubbing	Silicon tetrafluoride	>99%
		Hydrogen fluoride	>99%
		Phosphine	>99%
		Silane	>99.9%
	Oxidation using fuel	Silicon tetrafluoride	>99%
		Hydrogen fluoride	0%
		Phosphine	>99%
		Silane	>99%
	Oxidation using fuel/wet scrubbing	Silicon tetrafluoride	0%
		Hydrogen fluoride	0%
		Phosphine	>99.9%
		Silane	>99.9%
		Carbon monoxide	<1 lb/yr

Table 4-2. Compound Removal Efficiencies

Application / Process	Control Technology	Compound	Percent Removal Efficiency
			created
		Oxides of nitrogen	<3 lb/yr created
	Pre-pump reactor	Hydrogen fluoride	0%
		Phosphine	>99%
		Silane	>99%
		Silicon tetrafluoride	0%
	Wet scrubbing (with chemical addition)	Hydrogen fluoride	>99%
		Phosphine	0%
		Silane	80%
		Silicon tetrafluoride	>99%
Nitride deposition with silane; PFC clean  Gases fed: silane, ammonia	Cold bed	Ammonia	>99%
		Hydrogen fluoride	>99%
		Silane	>99%
		Silicone tetrafluoride	>99%
	Oxidation using electric/wet scrubbing	Ammonia	>99.9%
		Hydrogen fluoride	>99%
		Silane	>99.9%
		Silicone tetrafluoride	>99%
		Oxides of nitrogen	<20 lb/yr created
	Oxidation using fuel/wet scrubbing	Ammonia	>99%
		Hydrogen fluoride	>99%
		Silane	>98%
		Silicone tetrafluoride	>99%
		Carbon monoxide	<3 lb/yr created
		Oxides of nitrogen	<7 lb/yr created
	Pre-pump reactor	Ammonia	55 – 99%
		Hydrogen fluoride	0%
		Silane	>99%
		Silicone tetrafluoride	0%
		Oxides of nitrogen	0%
Wet scrubbing (with chemical addition)	Ammonia	>99%	
	Hydrogen fluoride	>99%	
	Silane	80%	
	Silicone tetrafluoride	>99%	
Nitride deposition with dichlorosilane; PFC clean	Cold bed	Ammonia	>99%
		Ammonia chloride	>99%
		Dichlorosilane	>99%
		Hydrogen fluoride	>99%

**Table 4-2. Compound Removal Efficiencies**

<b>Application / Process</b>	<b>Control Technology</b>	<b>Compound</b>	<b>Percent Removal Efficiency</b>
Gases fed: ammonia, dichlorosilane		Silicon tetrafluoride	>99%
	Hot chemical bed / ammonia control system	Ammonia	>99.9%
		Ammonia chloride	>99%
		Dichlorosilane	>99.9%
		Hydrogen fluoride	>99%
		Silicon tetrafluoride	>99%
	Oxidation using electric/wet scrubbing	Ammonia	>99.9%
		Ammonia chloride	>99%
		Dichlorosilane	>99%
		Hydrogen fluoride	>99%
		Silicon tetrafluoride	>99%
		Oxides of nitrogen	<25 lb/yr created
	Pre-pump reactor	Ammonia	55 – 99%
		Ammonia chloride	55 – 99%
		Dichlorosilane	>99%
		Hydrogen fluoride	0%
		Silicon tetrafluoride	0%
		Hydrogen chloride	Generated from dichlorosilane in pre-pump reactor
	Wet scrubbing (with chemical addition)	Ammonia	>99%
		Ammonia chloride	>99%
Dichlorosilane		>99.9%	
Hydrogen fluoride		>99%	
Silicon tetrafluoride		>99%	
Oxide deposition; PFC clean  Gases fed: silane, nitrous oxide	Cold bed	Hydrogen fluoride	>99%
		Silane	>99%
		Silicon tetrafluoride	>99%
	Hot chemical bed	Hydrogen fluoride	>99%
		Oxides of nitrogen	0%
		Silane	>99.9%
		Silicon tetrafluoride	>99%
	Oxidation using electric/wet scrubbing	Hydrogen fluoride	>99%
		Nitrous oxide	>50%
		Silane	>99.9%
		Silicon tetrafluoride	>99%
	Oxidation using fuel	Hydrogen fluoride	0%
		Silane	>98%
		Silicon tetrafluoride	0%

Table 4-2. Compound Removal Efficiencies

Application / Process	Control Technology	Compound	Percent Removal Efficiency
	Pre-pump reactor	Hydrogen fluoride	0%
		Nitrous oxide	28%
		Oxides of nitrogen	0%
		Silane	>99%
		Silicon tetrafluoride	0%
	Wet scrubbing (with chemical addition)	Hydrogen fluoride	>99%
		Nitrous oxide	0%
		Oxides of nitrogen	0%
		Silane	80%
		Silicon tetrafluoride	>99%
Tungsten Deposition; PFC clean  Gases fed: tungsten hexafluoride, silane	Cold bed	Hydrogen fluoride	>99%
		Silane	>99%
		Silicon tetrafluoride	>99%
		Tungsten hexafluoride	>99%
	Hot chemical bed	Hydrogen fluoride	>99%
		Silane	>99%
		Silicon tetrafluoride	>99%
		Tungsten hexafluoride	>99.9%
	Oxidation using electric/wet scrubbing	Hydrogen fluoride	>99%
		Silane	>95%
		Silicon tetrafluoride	>99%
		Tungsten hexafluoride	>99.9%
	Oxidation using fuel/wet scrubbing	Hydrogen fluoride	>99%
		Silane	>99%
		Silicon tetrafluoride	>99%
		Tungsten hexafluoride	>99%
		Carbon monoxide	<3 lb/yr created
		Oxides of nitrogen	<3 lb/yr created
	Pre-pump reactor	Hydrogen fluoride	0%
		Silane	>99%
		Silicon tetrafluoride	0%
		Tungsten hexafluoride	99%
		Wet scrubbing (with or without chemical addition)	Hydrogen fluoride
	Silane	80%	
Silicon tetrafluoride	>99%		

**Table 4-2. Compound Removal Efficiencies**

Application / Process	Control Technology	Compound	Percent Removal Efficiency
		Tungsten hexafluoride	99%
BPSG oxide deposition  Gases fed: silane, diborane, phosphine, nitrous oxide	Cold bed	Diborane	>99%
		Hydrogen fluoride	>99%
		Phosphine	>99%
		Silane	>99%
		Silicon tetrafluoride	>99%
	Hot chemical bed	Diborane	>99.9%
		Hydrogen fluoride	>99%
		Oxides of nitrogen	0%
		Phosphine	>99.9%
		Silane	>99.9%
	Oxidation using electric/wet scrubbing	Diborane	>99%
		Hydrogen fluoride	>99%
		Nitrous oxide	>41%
		Oxides of nitrogen	Not detected
		Phosphine	>99%
		Silane	>99.9%
	Oxidation using fuel	Diborane	>96%
		Hydrogen fluoride	0%
		Phosphine	>92%
		Silane	>95%
		Silicon tetrafluoride	0%
	Oxidation using fuel/wet scrubbing	Diborane	>99%
		Hydrogen fluoride	>99%
		Nitrous oxide	>99%
		Oxides of nitrogen	<3 lb/yr created
		Phosphine	>99%
		Silane	>99.9%
		Silicon tetrafluoride	>99%
Pre-pump reactor	Diborane	>99%	
	Hydrogen fluoride	0%	
	Nitrous oxide	28%	
	Oxides of nitrogen	0%	
	Phosphine	>99%	
	Silane	>99%	
	Silicon tetrafluoride	0%	

**Table 4-2. Compound Removal Efficiencies**

Application / Process	Control Technology	Compound	Percent Removal Efficiency
	Wet scrubbing (with or without chemical addition)	Diborane	99%
		Hydrogen fluoride	>99%
		Nitrous oxide	0%
		Oxides of nitrogen	0%
		Phosphine	0%
		Silane	80%
		Silicon tetrafluoride	>99%

Source: SEMATECH, 1997.

\* The removal efficiency of phosphine of 96% was reported by one supplier; however, no back-up information provided. Note: phosphine is only slightly soluble in water; therefore, minimal removal efficiency would be expected.

#### 4.2 Release from Container Residue

57. Industry practice is to return empty containers to the chemical supplier site for furthering processing. Environmental releases at the chemical supplier site are not within the scope of this ESD; however, Appendix C presents available information related to this release activity obtained through the development of the ESD.

#### 4.3 Release to Air or Water from Deposition Process (Release 1)

58. CVD precursors are used as starting materials for deposition of thin film. The CVD process involves vapour phase reactions; liquid precursors are transported to the wafer as a liquid/gas aerosol or via a vapourization chamber. During deposition, the precursors undergo a chemical reaction and are essentially intermediates that are destroyed in the process.

59. The quantity of unreacted material purged from the process chamber is related to the utilization rate of the precursor. Utilization is defined as the fraction of chemical consumed (reacted) during deposition, and is highly process-dependent. Information on material utilization rate is not publicly available because it is directly associated with production cost, which is considered proprietary information for semiconductor companies. One specialty chemical manufacturer estimates typical CVD precursor utilization rate to be in the 30 to 50 percent range (Industry, 2009). These are rough estimates based on engineering judgment and the company's knowledge of its customers (Industry, 2009). One literature source indicates that silane utilization rate in the industry could range from approximately 6 to 94 percent using plasma enhanced CVD<sup>13</sup>.

60. Due to high variability in utilization rate, chemical-specific data should always be used when available to estimate the amount of unreacted precursor

<sup>13</sup> J. Vac. Sci. Technol. A, Vol. 16, No. 3, pp. 1854-1855, May/June 1998.

remaining in the deposition chamber and vented to control technologies. In the absence of chemical-specific data, EPA recommends assuming 30 to 50 percent utilization rate for a given CVD precursor. Equation 4-2 calculates the quantity of a single precursor that is vented to POU control(s). The quantity should be presented as a range unless data are available to estimate chemical-specific utilization.

$$E_{\text{local}}_{\text{control}} = Q_{\text{chem\_site\_day}} \times (1 - U_{\text{process}}) \quad (4-1)$$

Where:

$E_{\text{local}}_{\text{control}}$	=	Daily release of chemical of interest to POU control (kg chemical released/site-day)
$Q_{\text{chem\_site\_day}}$	=	Daily use rate of chemical of interest (kg chemical/site-day) (Default: 2.8 kg/site-day; see Section 3.5)
$U_{\text{process}}$	=	Utilization rate of the CVD precursor (Default: 0.3 to 0.5 kg chemical consumed / kg chemical delivered to deposition chamber) (Industry, 2009)

61. Many CVD precursors are reactive, corrosive, and/or toxic themselves, or are used with hazardous gases (e.g. silane or hydrogen) that require POU abatement. Process chamber exhaust containing unreacted precursor is vented to POU controls, typically a thermal combustion system and/or a wet scrubber. The ESD assumes default POU abatement removal and destruction efficiency (EF) of 99 percent based on data presented in Table 4-2. The remaining one percent not destroyed by the POU is further routed to a central house abatement system, which could include on-site wastewater treatment or incineration system(s). As conservative, the ESD assumes releases from the central house control due to potential abatement inefficiencies. Equation 4-3 presents these “what-if” releases from the abatement systems:

$$E_{\text{local}}_{\text{process\_dsp}} = E_{\text{local}}_{\text{control}} \times (1 - \text{EF}) \quad (4-2)$$

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

Where:

$E_{\text{local}}_{\text{process\_dsp}}$	=	Daily release of chemical of interest to environment (kg chemical released/site-day)
$E_{\text{local}}_{\text{control}}$	=	Daily release of chemical of interest to control technology (kg chemical released/site-day)
EF	=	Efficiency of control technology (kg chemical captured/kg chemical vented to control technology) (Default: 0.99)

62. Potential release media include air or water. Where possible, chemical-specific information should be considered when determining the release media. Precursor chemicals that are pyrophoric (e.g. silane, phosphine, trimethyl aluminum) or flammable (e.g. ammonia, trimethylsilane, PDMAT, TDEAH, dichlorosilane, trichlorosilane, TEOS, TEB, and TDMAT) react readily in a thermal treatment unit. On the other hand, precursor chemicals that are water reactive (silicon tetrachloride, germanium tetrachloride, titanium tetrachloride, and tungsten hexafluoride) react readily with water in a scrubber system and are unlikely to have a subsequent water release (Airgard, 2014; CS Clean Systems, 2014; Edwards, 2014).

## 5 OCCUPATIONAL EXPOSURE ASSESSMENTS

63. Semiconductor manufacturing processes differ significantly from typical chemical manufacturing processes. The production of semiconductor wafers occurs in a clean room environment with stringent controls. Furthermore, semiconductor CVD precursors are used in a closed system with multiple controls in place to prevent worker exposure. As such, exposure to CVD precursors is expected to be negligible during CVD operations. This section discusses the PPE and engineering controls used at semiconductor sites.

64. Appendix D presents methods for estimating exposures at the chemical supplier site, which is outside the scope of this ESD.

### 5.1 Personal Protective Equipment

65. Due to the cleanliness requirements at semiconductor manufacturing facilities, all production workers entering the production floor are required to wear clean room suits, an overall garment consisting of a coverall, fitted cap, face cover, gloves, and booties. The clean room suits prevent skin and hair from shedding into the clean room. In addition to these suits, PPE such as safety glasses, goggles, and chemical protective gear may also be worn on an as-needed basis.

66. Most semiconductor manufacturers require that newly purchased process equipment undergo a SEMI S-2 assessment<sup>14</sup>. The SEMI S-2 guideline was first published in 1991 to create a common set of environmental, health and safety requirements for semiconductor process tools. S-2 addresses environmental considerations, interlocks, exhaust ventilation, chemicals and other safety and health topics. The guidelines call for equipment to be designed such that there is no chemical exposure to the workplace environment during normal operation (worst case ambient concentrations must be less than 1 percent of the occupational exposure limit, OEL) while emissions during equipment maintenance and equipment failures must be less than 25 percent of the OEL.

### 5.2 Number of Workers at the Semiconductor Manufacturing Site

67. According to the 2011 U.S. Census Bureau's, there are 922 semiconductor facilities in the United States under NAICS code 334413<sup>15</sup> (e.g. Semiconductor and Related Device Manufacturing), employing a total of 98,386 people. Each facility

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<sup>14</sup><http://ams.semi.org/ebusiness/standards/SEMISTandardDetail.aspx?ProductID=1948&DownloadID=2766>

<sup>15</sup> 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].

employs 107 workers<sup>16</sup> on average (USCB, 2011b). Some of these employees are not expected to work in the production areas. The *2011 Annual Survey of Manufacturers* (ASM) estimates that approximately 58 percent of the workers within this NAICS code are *production* workers (USCB, 2011b), 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, 2011b].*

68. Additionally, the establishments listed in the Census include smaller semiconductor establishments (e.g. sales offices, warehouses, etc) that are unlikely to be manufacturing facilities. Table 5-1 shows the distribution of facilities and employees, based on the employment-size class (e.g. the number of employees at each facility) that fall under NAICS code 334413. According to SIA, “it is unlikely that any facility with less than 50 employees could support semiconductor manufacturing;” therefore, those establishments with less than 50 employees should not be considered when determining the total number of semiconductor manufacturing establishments (SIA, 2003). Excluding these facilities, Census data report an average of 373 employees or 187 production workers employed at each facility (USCB, 2011b).

69. Furthermore, a typical semiconductor facility operates between 6 and 11 major processes (Shah, 2006). Therefore, only a portion of the production workers described by the U.S. Census data are involved in the CVD process. Recent information obtained through contacts with individuals with experience in the semiconductor industry suggests no more than 10 percent of all production workers at a single facility are involved in CVD operations (Shah, 2009). Therefore, *approximately 19 production workers per facility* on average could be involved in CVD. None of these production workers would be exposed to CVD precursors.

70. Because workers at the semiconductor facility are dedicated to one specific process area, the number of workers involved in CVD differs from the number of

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<sup>16</sup> 2007 Census data report an average of 162 employees per establishment for this NAICS code – a slight increase from the 2004 value (Census, 2007). However, 2007 data are not used because they provide insufficient detail on the size of these facilities.

workers involved in photolithography. Therefore, the number of workers per site estimate in this ESD differs from that in the OECD Environment, Health and Safety Publications Series on Emission Scenario Documents No. 9: *Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing* (OECD, 2010)<sup>17</sup>.

**Table 5-1. 2011 Census Data on the Number of U.S. Facilities and Employees by Employment-Size Class for the Semiconductor and Related Device Manufacturing Industry Sector (NAICS 334413)**

<b>Employment-Size Class</b>	<b>1-4</b>	<b>5-9</b>	<b>10-19</b>	<b>20-49</b>	<b>50-99</b>	<b>100-249</b>	<b>250-499</b>	<b>500-999</b>	<b>≥1,000</b>	<b>Total</b>
Number of Facilities (% of total)	285 (31%)	132 (14%)	130 (14%)	131 (14%)	68 (7%)	82 (9%)	44 (5%)	33 (4%)	17 (2%)	922 (100%)
Number of Employees (% of total)	478 (0.5%)	885 (0.9%)	1,838 (2%)	4,104 (4%)	4,753 (5%)	12,532 (13%)	16,404 (17%)	21,833 (22%)	35,559 (36%)	98,386 (100%)

Source: USCB, 2011b.

Note: more detailed facility and employee distribution information is available at USCB, 2011b (see Section 8). The percentages may not add up to 100 due to rounding.

### 5.3 Potential for Exposure during Container Cleaning

71. As an industry practice, empty CVD precursor containers are shipped back to the supplier for cleaning and refilling. Therefore, there is no worker exposure associated with container cleaning at the semiconductor manufacturing site.

72. Appendix D presents available information on worker exposure during container cleaning at the chemical supplier site, including the number of workers, and methods for estimating dermal and inhalation exposures. Note worker exposure at the supplier site is outside the scope of this ESD. EPA recommends users of this ESD to reference PMN submissions to address the potential for worker exposure at chemical supplier sites.

### 5.4 Potential for Exposure during Equipment Maintenance and Other Activities at Semiconductor Manufacturing Sites

73. The production of semiconductor wafers occurs in a clean room with stringent controls that mitigate exposures. Newer semiconductor facilities use totally enclosed processes, automation, and chemical delivery systems to physically remove workers from hazardous materials. Specifically, CVD is done through vacuums, consisting of an internal reactor, collecting surface, gas delivery system, energy

<sup>17</sup> This ESD estimates 48 equipment operators and 18 technicians are potentially exposed to photoresist (OECD, 2010).

source, substrate loading mechanism, exhaust system, process control equipment, and the substrate (Semi-Directory, 2010). Worker exposure to CVD precursors are not expected at these facilities because extensive controls, leak detection, and integrated safety locks are in place (Shah, 2008):

- **Raw Material (CVD precursor) Loading and Unloading:** Transport containers are located in a separate supply cabinet. Before an empty container/cylinder can be removed from the supply cabinet (or after a new container has been hooked up to the system), the connectors must be first purged free of any residual chemical. This can be done using either a pump and purge procedure or a liquid solvent rinse. After purging, the precursor is transported to the chamber via automated gas delivery system equipped with pressure monitors. Cabinet fires due to spilled or leaking pyrophoric chemicals are prevented by constant nitrogen over-pressure. In the event of leakage, a nitrogen shower is activated to deplete oxygen levels (CS Clean Systems, undated);
- **CVD Process:** Deposition takes place inside a heated chamber under vacuum. Workers are not exposed to chemicals during deposition;
- **CVD Chamber Cleaning:** Cleaning takes place inside a vacuum environment where cleaning gases are delivered via automation. Workers are not exposed to cleaning chemicals (outside the scope of this ESD);
- **Chamber Maintenance:** Manual intervention may be occasionally required. However, chambers are purged free of any precursor and hazardous material prior to human entry.

74. Because high chemical purity and tight process controls are critical in achieving the desired deposition conditions and film quality (MKS Instruments, 2006), engineering controls are expected to be used to prevent any process leaks. These controls in turn minimize exposure. There is no opportunity for direct, routine handling of or exposure to CVD precursor during semiconductor manufacturing. Worker monitoring conducted in 2012 and compiled by SIA/ISMI further confirms that worker exposure is negligible. Of the 24 data points available, the CVD precursor concentration in air was below the detection limit for all measurements (Industry, 2014). See Appendix E.

75. Note the OECD ESD on *Photoresist Use* assesses dermal exposure to photoresist at semiconductor manufacturing site. The difference in exposure assessments between the two ESDs is due to fundamental differences between the photolithography and the CVD processes, and the types of chemicals used. Because CVD precursors are likely to present more health and safety hazards, additional controls are implemented to prevent exposure to these chemicals.

## 6 SAMPLE CALCULATIONS

76. This section presents an example of how the equations described in Sections 3 through 5 may be used to estimate releases of and exposures to a CVD precursor used in semiconductor processes. 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. Sample calculations are based on the following assumptions:

1. Precursor chemical production volume ( $Q_{\text{chem\_yr}}$ ) is *10,000 kg chemical/yr*.
2. Precursor chemical is a liquid and is received at semiconductor manufacturing sites as a pure substance, or 100 percent by weight ( $F_{\text{chem}} = 1.0$ ).
3. The end use of the precursor is estimated to occur at 10 sites.

### 6.1 General Facility Estimates

#### 6.1.1 Days of Operation ( $TIME_{\text{operating\_days}}$ )

77. If specific information is not available to estimate the days of operation ( $TIME_{\text{operating\_days}}$ ) at a semiconductor manufacturing site, a default value of 360 days per year should be assumed.

#### 6.1.2 Daily Use Rate of CVD Precursor ( $Q_{\text{chem\_site\_day}}$ )

78. The daily use rate of a CVD precursor can be estimated using Equation 3-1:

$$Q_{\text{chem\_site\_day}} = \frac{Q_{\text{chem\_site\_yr}}}{TIME_{\text{working\_days}}} \quad (3-1)$$

$$Q_{\text{chem\_site\_day}} = \frac{1,000\text{kg}}{\text{site} \cdot \text{yr}} \times \frac{\text{yr}}{360 \text{ day}} = 2.8 \frac{\text{kg}}{\text{site} \cdot \text{day}}$$

Where:

$Q_{\text{chem\_site\_day}}$  = Daily use rate of CVD precursor (kg/site-day)

$Q_{\text{chem\_site\_yr}}$  = Annual use rate of CVD precursor  
(Default: 1,000 kg/site-yr)

$TIME_{\text{operating\_day}}$  = Number of operating days at semiconductor manufacturing site (Default: 360 days/yr)

#### 6.1.3 Number of Sites ( $N_{\text{sites}}$ )

79. The number of semiconductor manufacturing facilities using the chemical of interest ( $N_{\text{sites}}$ ) can be estimated using Equation 3-2:

$$N_{\text{sites}} = \frac{Q_{\text{chem\_yr}} \times (1 - F_{\text{container\_disp}})}{Q_{\text{chem\_site\_day}} \times \text{TIME}_{\text{operating\_days}}} \quad (3-2)$$

$$N_{\text{sites}} = 10,000 \frac{\text{kg}}{\text{yr}} \times (1 - 0.006) \times \frac{\text{day}}{2.8 \text{ kg}} \times \frac{\text{yr}}{360 \text{ day}}$$

$$N_{\text{sites}} = 10 \text{ sites}$$

Where:

$N_{\text{sites}}$	=	Number of sites using the precursor chemical (sites)
$Q_{\text{chem\_yr}}$	=	Annual production volume of precursor chemical (kg chemical/yr)
$Q_{\text{chem\_site\_day}}$	=	Daily use rate of CVD precursor (kg chemical/site-day)
$\text{TIME}_{\text{working\_days}}$	=	Number of operating days at semiconductor manufacturing sites (days/yr) (Default: 360 days/yr)

80. The estimate is consistent with the assumption of 10 end-use sites.

#### 6.1.4 Number of Transport Containers Unloaded per Site ( $N_{\text{container\_unload\_site\_yr}}$ )

##### 6.1.4.1 Liquid

81. The number of transport containers unloaded annually per site can be estimated based on the daily use rate, container size, and the purity of the precursor:

$$N_{\text{container\_unload\_site\_yr}} = \frac{Q_{\text{chem\_site\_day}} \times \text{TIME}_{\text{operating\_days}}}{F_{\text{chem}} \times V_{\text{container}} \times \rho_{\text{formulation}}} \quad (3-3)$$

$$N_{\text{container\_unload\_site\_yr}} = 2.8 \frac{\text{kg}}{\text{site} \cdot \text{day}} \times \frac{360 \text{ day}}{\text{yr}} \times \frac{1 \text{ kg formulation}}{1 \text{ kg chemical}} \times \frac{\text{container}}{60.6 \text{ L}} \times \frac{\text{L}}{1 \text{ kg formulation}}$$

$$N_{\text{container\_unload\_site\_yr}} = 17 \frac{\text{container}}{\text{site} \cdot \text{yr}}$$

Where:

$N_{\text{container\_unload\_site\_yr}}$	=	Number of transport containers unloaded at each site per year (containers/site-yr)
$Q_{\text{chem\_site\_day}}$	=	Daily use rate of CVD precursor (kg/site-day)
$F_{\text{chem}}$	=	Weight fraction of precursor in the formulation as received (Default: 1 kg chemical/kg formulation)
$\text{TIME}_{\text{operating\_days}}$	=	Number of operating days (days/yr) (Default: 360 days/yr)
$V_{\text{container}}$	=	Volume of transport container (Default: 60.6 L container)
$\rho_{\text{formulation}}$	=	Density of chemical formulation (assumed 1kg/L for liquids)

## 6.1.4.2 Gas

82. While the method for calculating the number of transport containers applies to all physical forms, the default density ( $\rho_{\text{formulation}}$ ) differs for liquid and gas. This ESD recommends a default density of 0.52 kg/L for gaseous substances based on available packaging information for compressed trimethylsilane. When the critical temperature and pressure of the precursor are known, users of this ESD are encouraged to refer to Appendix B to more accurately estimate the density of the chemical of interest.

83. Assuming the chemical of interest has a critical temperature of 132°C, a critical pressure of 112.8 bar and a molecular weight of 32 g/mol, the reduced temperature and pressure can be calculated to determine the compressibility factor:

$$T_r = \frac{T}{T_c} = \frac{293\text{K}}{(132 + 273)\text{K}} = 0.72$$

$$P_r = \frac{P}{P_c} = \frac{103\text{bar}}{112.8\text{bar}} = 0.91$$
(C-3)

$z \sim 0.15$  (see Figure C-1)

Where:

$P_r$	=	Reduced pressure (Default: 103 bar)
$P_c$	=	Critical pressure
$T_r$	=	Reduced temperature (Default: 293K or 20°C)
$T_c$	=	Critical temperature
$z$	=	Compressibility factor (dimensionless)

84. Subsequently, the density of the compressed gas can be calculated using Equation C-2<sup>18</sup>.

$$\rho_{\text{formulation}} = \frac{MW_{\text{chem}}}{\tilde{V}} = \frac{MW_{\text{chem}} \cdot P}{z \cdot RT} = 0.032 \frac{\text{kg}}{\text{mol}} \cdot \frac{103\text{ bar}}{0.15 \cdot 293\text{ K}} \cdot \frac{\text{mol} \cdot \text{K}}{0.08314\text{ L} \cdot \text{bar}}$$
(C-2)

$$\rho_{\text{formulation}} = 0.90 \frac{\text{kg}}{\text{L}}$$

Where:

$\tilde{V}$	=	Molar volume (L/mol)
$P$	=	Pressure (bar <sup>19</sup> )
$R$	=	Universal gas constant (0.08314 L-bar/mol-K)
$T$	=	Temperature (K)
$MW_{\text{chem}}$	=	Molecular weight of chemical of interest (kg/mol)

<sup>18</sup> Actual net weight of chemical inside the container, when available, should be used to calculate the number of containers instead of the equations shown in this section.

<sup>19</sup> Available information indicates that silanes are packaged at up to 1500 psi (103 bar) (Air Products, 2008).

85. The number of containers can then be calculated using Equation 3-3:

$$N_{\text{container\_unload\_site\_yr}} = 2.8 \frac{\text{kg}}{\text{site} \cdot \text{day}} \times \frac{360 \text{ day}}{\text{yr}} \times \frac{1 \text{ kg formulation}}{1 \text{ kg chemical}} \times \frac{\text{container}}{60.6 \text{ L}} \times \frac{\text{L}}{0.90 \text{ kg formulation}}$$

$$N_{\text{container\_unload\_site\_yr}} \sim 19 \frac{\text{container}}{\text{site} \cdot \text{yr}}$$

## 6.2 Environmental Releases

### 6.2.1 Release to Air or Water from Deposition Process (Release 1)

86. The amount of unutilized precursor that passes to POU abatement can be calculated using the following equation:

$$\text{Elocal}_{\text{control}} = Q_{\text{chem\_site\_day}} \times (1 - U_{\text{process}}) \quad (4-1)$$

$$\text{Elocal}_{\text{control}} = \frac{2.8 \text{ kg}}{\text{site} \cdot \text{day}} \times [1 - (0.3 \text{ to } 0.5)] = \frac{1.4 \text{ kg}}{\text{site} \cdot \text{day}} \text{ to } \frac{2.0 \text{ kg}}{\text{site} \cdot \text{day}}$$

87. The amount of precursor that passes through POU abatement and routed to central house abatement can be calculated using the following equation. This amount could result in an ultimate release to the environment depending on the type and efficiency of central house abatement system.

$$\text{Elocal}_{\text{process\_disp}} = \text{Elocal}_{\text{control}} \times (1 - \text{EF}) \quad (4-2)$$

$$\text{Elocal}_{\text{process\_disp}} = \left( \frac{1.4 \text{ kg}}{\text{site} \cdot \text{day}} \text{ to } \frac{2.0 \text{ kg}}{\text{site} \cdot \text{day}} \right) \times (1 - 0.99) = \frac{0.014 \text{ kg}}{\text{site} \cdot \text{day}} \text{ to } \frac{0.02 \text{ kg}}{\text{site} \cdot \text{day}}$$

88. This release will occur over 360 day/year from each of 10 sites.

Media of release: Air or water.

## 6.3 Occupational Exposures

89. None. Worker exposure is expected to be negligible at the semiconductor site.

## **7 DATA GAPS/UNCERTAINTIES AND FUTURE WORK**

90. During the development of this ESD, a comprehensive literature search was conducted to obtain information on general facility estimates, release estimates, and exposure estimates. The ESD was further enhanced through consultation with industry trade associations and their member companies. The ESD incorporates the industry comments received, including detailed information regarding semiconductor processes, engineering controls and abatement, abatement destruction and removal efficiency, and worker exposure. It is believed the ESD provides a conservative risk-screening assessment approach, and reflects current industry practices at the time of ESD development.

91. Moving forward, additional industry data are welcomed so that the ESD can be as up-to-date as possible. Reviewers should also feel free to recommend additional resources that may further enhance this ESD.

## 8 REFERENCES

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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 Section 3, which are used to calculate the general facility parameters. Table A-2 and A-3 summarize the equations used in evaluating releases of and exposures to CVD precursors used in semiconductor manufacturing. 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. General Facility Parameter Calculation Summary**

<b>General Facility Estimates</b>	
<b>Daily Use Rate of CVD Precursor (kg/site-day), <math>Q_{chem\_site\_day}</math>:</b>	
$Q_{chem\_site\_day} = \frac{Q_{chem\_site\_yr}}{TIME_{operating\_days}} \quad (\text{Eqn. 3-1})$	
<b>Number of Sites (<math>N_{sites}</math>):</b>	
$N_{sites} = \frac{Q_{chem\_yr} \times (1 - F_{container\_disp})}{Q_{chem\_site\_day} \times TIME_{operating\_days}} \quad (\text{Eqn. 3-2})$	
<b>Number of Transport Containers Unloaded per Site, <math>N_{container\_unload\_site\_yr}</math>:</b>	
$N_{container\_unload\_site\_yr} = \frac{Q_{chem\_site\_day} \times TIME_{operating\_days}}{F_{chem} \times V_{container} \times \rho_{formulation}} \quad (\text{Eqn. 3-3})$	

**Table A-2. Environmental Release Calculation Summary**

Source	Possible Medium	Daily Release Rates (kg/site-day), Elocal (for Given Sources)
Deposition Process	Air, wastewater treatment, incineration	$Elocal_{control} = Q_{chem\_site\_day} \times (1 - U_{process}) \quad (\text{Eqn. 4-1})$ $Elocal_{process\_disp} = Elocal_{control} \times (1 - EF) \quad (\text{Eqn. 4-2})$ <p>This release will occur over <math>[TIME_{operating\_days}]</math> days/year from <math>[N_{sites}]</math> sites.</p>

**Table A-3. Occupational Exposure Calculation Summary**

<b>Occupational Exposure Calculations</b>
<b>Number of Workers Exposed Per Site:</b> Up to 19 workers per semiconductor manufacturing site (USCB, 2004a; SIA, 2003).
None

**Table A-4. Parameter Declaration and Documentation Summary**

<b>Variable</b>	<b>Variable Description</b>	<b>Default Value</b>	<b>Data Source</b>
EF	Efficiency of control technology	0.99	SEMATECH, 1997
E <sub>local<sub>control</sub></sub>	Daily release of the chemical to control technology (kg chemical/site-day)	Calculated	Section 4.4
E <sub>local<sub>process_disp</sub></sub>	Daily release of the chemical to the environment, after control technology (kg chemical/site-day)	Calculated	Section 4.4
F <sub>chem</sub>	Weight fraction of CVD precursor in formulation supplied to end user	1	Industry, 2009-2010
F <sub>container_disp</sub>	Fraction of the precursor chemical remaining in the emptied container (kg chemical remaining/kg chemical in full container)	0.1	CEB, 2002
MW <sub>chem</sub>	Molecular weight of the CVD precursor (g/mol)	Chemical Specific	Manufacturer
N <sub>container_unload_site_yr</sub>	Number of transport containers unloaded at each site per year (containers/site-yr)	Calculated	Section 3.7
N <sub>exp_incident</sub>	Number of exposure incidents per day (incidents/day)	1	CEB, 2000
N <sub>sites</sub>	Number of sites using the CVD precursor (sites)	Calculated	Section 3.6
Q <sub>chem_site_day</sub>	Daily use rate of CVD precursor (kg chemical/site-day)	Calculated	Section 3.5
Q <sub>chem_yr</sub>	Annual production volume of CVD precursor (kg chemical/yr)	Chemical Specific	Manufacturer
Q <sub>chem_site_yr</sub>	Annual use rate of CVD precursor (kg chemical/site-yr)	1,000	Industry, 2009

<b>Variable</b>	<b>Variable Description</b>	<b>Default Value</b>	<b>Data Source</b>
$\rho_{\text{formulation}}$	Density of the chemical formulation containing CVD precursor (kg formulation/L formulation)	1 (liquid) 0.52 (gas)	EPA assumption
$\text{TIME}_{\text{operating\_days}}$	Total facility operating days (days/yr)	360	SIA, 2003
$U_{\text{process}}$	Utilization rate of the CVD precursor (dimensionless)	0.3 – 0.5	Industry, 2009
$V_{\text{container}}$	Volume of transport container (L/container)	60.6	Shah, 2010
$\text{VP}_{\text{chem}}$	Vapour pressure of the CVD precursor (torr)	Chemical Specific	Manufacturer
$\text{VP}_{\text{k}}$	Vapour pressure of the known chemical (torr)	Chemical Specific	Manufacturer
$X_{\text{chem}}$	Mole fraction of the CVD precursor (dimensionless)	1	EPA assumption
$X_{\text{k}}$	Mole fraction of the known chemical (dimensionless)	1	EPA assumption

**APPENDIX B**

**METHODS FOR DETERMINING THE DENSITY OF COMPRESSED  
GASEOUS PRECURSORS**

Equation 3-3 of this ESD calculates the number of transport containers (cylinders) unloaded annually per site. The use of this equation requires knowledge of the density of the chemical of interest,  $\rho_{\text{formulation}}$ . While the density is chemical-specific, this physical property information is expected to be readily-available for most substances. For liquids, this ESD assumes a default density of 1 kilogram per liter, which is the density of water.

Because gaseous substances are expected to be packaged as compressed gases or pressurized liquids, it is not appropriate to assume the gases remain at standard conditions (atmospheric temperature and pressure) for this calculation. Using the density of these substances at standard conditions would result in significant overestimation on the number of containers. This Appendix provides two alternate methods for estimating the density of gaseous substances inside pressurized containers.

### Method 1: ESD Default

According to Air Products' product description, the standard packaging for trimethylsilane – a common precursor used in CVD – is a X49S cylinder with an internal volume of 49.8 liters and a fill weight of 26 kilograms (Air Products, 2006). The density of trimethylsilane can simply be determined by dividing the mass by the volume.

$$\rho_{\text{formulation}} = \frac{m}{V_{\text{container}}} \quad (\text{B-1})$$

$$\rho_{\text{formulation}} = \frac{26 \text{ kg}}{49.8 \text{ L}} = 0.52 \frac{\text{kg}}{\text{L}} \text{ (trimethylsilane)}$$

Where

$\rho_{\text{formulation}}$	=	Density of chemical of interest (kg/L)
$m$	=	Mass of chemical of interest inside container (kg)
$V_{\text{container}}$	=	Volume of container (L)

Because information on standard packaging for other common precursors is not available, the density of 0.52 kg/L is used as default for this ESD. This default value assumes the gaseous precursor is pressurized as a liquid in the transport container. It is important to note that the density would vary depending on the chemical's physical characteristics, packaging conditions, and transport container. Users of this ESD are encouraged to calculate an alternate value using Equation B-1 when chemical-specific information is available.

### Method 2: Equation of State and Compressibility Factor

Density (or molar volume) of a gas is a function of temperature and pressure. At low pressure or high temperature, the density can be estimated using the Ideal Gas Law. However, the Ideal Gas Law neglects the volume occupied by the molecules and intermolecular forces among the molecules, and is not applicable to gaseous

substances packaged in pressurized containers. In this situation, an alternate equation of state must be used to account for this deficiency. The generalized equation of state, as defined below, introduces a correction factor “z” that accounts for deviation from ideal gas behavior (Seader and Henley, 1998):

$$P\tilde{V} = z \cdot RT \quad \text{or} \quad \tilde{V} = \frac{z \cdot RT}{P} \quad (\text{B-2})$$

$$\rho_{\text{formulation}} = \frac{\text{MW}}{\tilde{V}}$$

Where:

$\tilde{V}$	=	Molar volume (L/mol)
P	=	Pressure (bar <sup>20</sup> )
z	=	Compressibility factor (dimensionless)
R	=	Universal gas constant (0.08314 L-bar/mol-K)
T	=	Temperature (K)
MW	=	Molecular weight of chemical of interest (kg/mol)

The compressibility factor is a function of the reduced temperature and reduced pressure, which are defined as:

$$T_r = \frac{T}{T_c} \quad \text{and} \quad (\text{B-3})$$

$$P_r = \frac{P}{P_c}$$

Where:

$P_r$	=	Reduced pressure
$P_c$	=	Critical pressure
$T_r$	=	Reduced temperature
$T_c$	=	Critical temperature

One common method to determine the compressibility factor, based on the reduced temperature and pressure, is to use the normalized compressibility chart, as shown in Figure B-1.

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<sup>20</sup> Available information indicates that silanes are packaged at up to 1500 psi (103 bar) (Air Products, 2008).

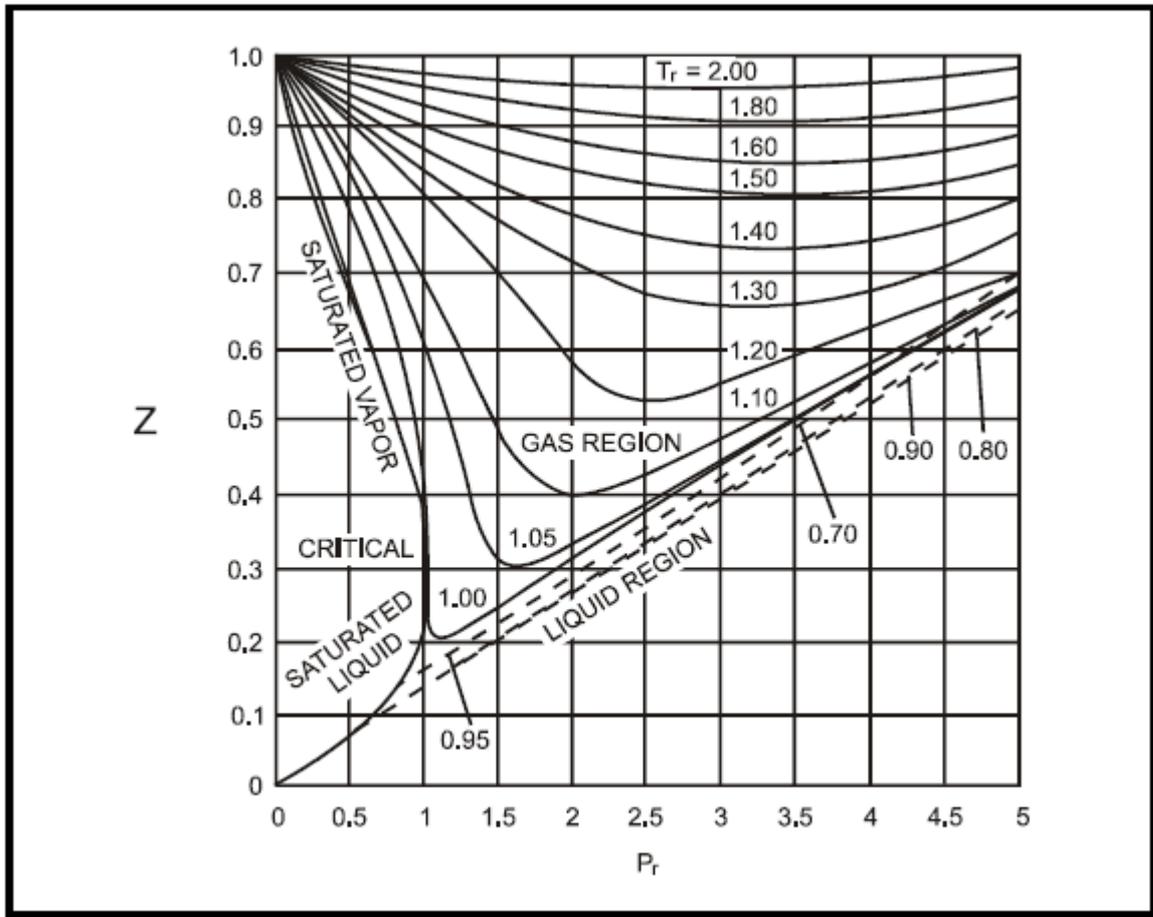


Figure 3-6. Compressibility Chart (High Range)  
(Courtesy of Fischer & Porter)

**Figure B-1. Compressibility Chart (High Range).**

The reduced temperature and pressure are calculated based on the critical points of a chemical. When information on critical points is available, users of this ESD are encouraged to estimate the compressibility factor using the above compressibility chart. The molar volume and the density of the compressed gas can be subsequently determined using Equation B-2. Table B-1 presents the estimated reduced temperature and pressure at 103 bar and 293K, the compressibility factor, molar volume, and density for several compressed gases that are commonly used for deposition.

**Table B-1. Compressibility Factor and Density of Several Common CVD Precursors at 103 bar and 293 K (20°C)**

Chemical	$T_r$	$P_r$	$z$	Molar Volume (L/mol)	MW (g/mol)	$\rho$ (kg/L)
NH <sub>3</sub>	0.72	0.91	0.15	0.035	32	0.90
PH <sub>3</sub>	0.90	1.58	0.21	0.050	33.4	0.66
WF <sub>6</sub>	0.66	2.41	0.32	0.076	297.8	3.92
SiH <sub>4</sub>	1.09	2.13	0.40	0.095	32.1	0.34
(CH <sub>3</sub> ) <sub>3</sub> SiH	0.68	3.30	0.46	0.109	74.2	0.68

**APPENDIX C**

**ENVIRONMENTAL RELEASES AT THE CHEMICAL SUPPLIER SITE**

## Releases to Water, Incineration, or Landfill from Container Residue

CVD precursors are usually gases, liquefied compressed gases, or liquids. Liquid precursors are supplied in bubblers, canisters, and bulk containers with sizes ranging from less than 1 liter to up to 50 liters (Air Liquide Technology, undated). In some cases (e.g. tetraethylorthosilicate (TEOS)), liquid precursors are supplied in larger containers ranging from 19 to 250 liters (REACH, 2010). Gases and liquefied gases are supplied in cylinders and bulk containers such as tube trailers and ISO containers. The selection of the container material depends on the chemical and physical properties of the chemical; for example, carbon steel cylinders can be used for virtually every compressed gas while stainless steel cylinders are commonly used to package gases for special applications (e.g.  $WF_6$ ). Electroless nickel coating carbon steel cylinders are primarily used to package corrosive materials while aluminum containers have limited uses but are light-weight and provide a clean interior (Air Liquide Technology, undated). Bubblers and canisters can be stainless steel or quartz.

Based on information obtained from several specialty chemical suppliers, containers used to transport CVD precursors are typically returned to the manufacturers for cleaning and refilling (Industry, 2009). Table C-1 summarizes types and sizes the precursor containers, typical residue in the returned container, empty container handling practices, and typical risk management measures used to minimize environmental release and worker exposure.

Bubblers and canisters for liquid precursors are typically cleaned using custom designed equipment under three major steps: 1) the container is moved inside an inert atmosphere dry box or closed, exhausted environment and the residual chemical is gravity drained or flushed from the container with an inert solvent to a small stainless steel tank; 2) the container, now inert and containing no hazardous materials, may be attached to another custom built processing station where the interior is washed with three different solvents and water; and 3) the container is washed again in an ultrasonic bath in a class 100 clean room environment to remove any trace particles and dried (Industry, 2009). Empty containers are then refilled. In the vast majority of cases, refilling is done within a closed environment, but it could be done in an open, exhausted hood. Bulk canisters are typically drained and then refilled, with solvent cleaning and drying occurring in some cases (Industry, 2013).

Venting, evacuating, and then purging with inert gas is the predominant approach of residue removal from gas cylinders. Cylinders and connection points are contained in enclosed, ventilated systems with air flow velocities dependent on the hazard of the chemical. After material has been removed, samples are taken from the container for analysis (GC, FTIR, capacitance  $H_2O$  or  $O_2$ , etc) to check against specification and to determine that no additional contamination has been introduced during use. If none is detected, the gas cylinder is refilled without cleaning. For liquefied gases, a heat treatment step may be used (or purge gas heated) to aid in removal of residual material. Analysis is repeated after filling.

The process of “top filling” gases onto residual material is not normally permitted because of the possibility of cross contamination. Whenever possible, the unused residue is returned to commercial use.

During the development of this ESD, SIA and SEMATECH sent a survey to three major suppliers of specialty chemicals, including CVD precursors, to obtain information on the disposal of container residue and the receiving environmental media. Table C-2 presents available information on container residue disposal and the associated release media. The control technology efficiency at the chemical supplier site should be considered when evaluating environmental releases during container cleaning.

Table C-1. Precursor Container Sizes, Residue, RMM, and Handling

Precursor State	Container Type	Container Size (kg)	Typical Amount of Residue in Container	Typical Empty Container Handling Procedure	Typical Risk Management Measures to Prevent Worker Exposure	Typical Handling/Disposal of CVD precursor residue	Typical Air Emissions Abatement	Typical Abatement Efficiency (% Destruction-removal efficiency)
Gas	Gas Cylinder	1-15	5-10%	<ol style="list-style-type: none"> <li>1) Cylinder is vented/purged with inert gas.</li> <li>2) Cylinder is sampled to ensure no contamination.</li> <li>3) Empty cylinder is refilled.</li> </ol>	Cleaning operations performed in closed systems. Cylinder and connection points in ventilated spaces with air flow velocities dependent on hazard class of chemical. Ventilated spaces are monitored. PPE dependent on specific chemical hazards. Vacuum exhaust and purge gas exhaust are directed to a specific process scrubber which is backed up by a plant scrubber which is monitored.	When possible, the unused commercial product is returned to commercial use. Waste directed to appropriate treatment including thermal oxidation + filter, reaction with water, adsorption and oxidation. Solids sent to landfill.	Flammable = combustion + filter; solid collection to landfill. Corrosive = reaction with water to water discharge. Hydrides of As = adsorbent + oxidation; solid collection to landfill.	>99%
Liquefied Gas	Gas Cylinder	5-15	1-10%	<ol style="list-style-type: none"> <li>1) Cylinder or purge gas is heated.</li> <li>2) Cylinder is vented/purged.</li> <li>3) Cylinder is sampled to ensure no contamination.</li> <li>4) Empty cylinder is refilled.</li> </ol>	Cleaning operations performed in closed systems. Cylinder and connection points in ventilated spaces with air flow velocities dependent on hazard class of chemical. Ventilated spaces are monitored. PPE dependent on specific chemical hazards. Vacuum exhaust and purge gas exhaust are directed to a specific process scrubber which is backed up by a plant scrubber which is monitored.	When possible, the unused commercial product is returned to commercial use. Waste directed to appropriate treatment including thermal oxidation + filter, reaction with water, adsorption and oxidation. Solids sent to landfill.	Flammable = combustion + filter; solid collection to landfill. Corrosive = reaction with water to water discharge.	>99%
Gas or Liquefied Gas	Bulk Container - tube trailer, ISO modules	100-4,500	2-10%	<ol style="list-style-type: none"> <li>1) Purge gas is heated.</li> <li>2) Container is vented/purged.</li> <li>3) Container is sampled to ensure no contamination.</li> <li>4) Empty container is refilled.</li> </ol>	Cleaning operations performed in closed systems. Bulk Container connection points in ventilated spaces with air flow velocities dependent on hazard class of chemical. Ventilated spaces are monitored. PPE dependent on specific chemical hazards. Vacuum exhaust and purge gas exhaust are directed to a specific process scrubber which is backed up by a plant scrubber which is monitored.	When possible, the unused commercial product is returned to commercial use. Waste directed to appropriate treatment including thermal oxidation + filter, reaction with water, adsorption and oxidation. Solids sent to landfill.	Flammable = combustion + filter; solid collection to landfill. Corrosive = reaction with water to water discharge.	>99%
Liquid	Bubbler/Canister	1-200	5-10%	<ol style="list-style-type: none"> <li>1) Container is moved to glove box or other enclosed and ventilated environment equipped with monitoring and alarms when needed.</li> <li>2) Residual chemical is gravity drained or flushed from the container.</li> <li>3) Empty container may be moved to closed process station where interior is rinsed with multiple solvents.</li> <li>4) Trace particles are removed in an ultrasonic bath.</li> </ol>	Process occurs in glove box or in well ventilated, hooded enclosure. Most processing occurs in closed system. Equipped with local area monitors and alarms when needed. Worker PPE includes lab coat, gloves, safety glasses; in some cases a face shield is worn. Respiratory protection is utilized for non-standard returns processing.	When possible, the unused commercial product is returned to commercial use. When solvent flush utilized, waste flush solvent + chemical is sent for off-site combustion. Exhaust from glovebox sent to plant combustion scrubber.	Flammable = combustion and filter collection; solid by-products to landfill. In some cases, process exhaust trapped in closed systems and sent for off-site combustion.	>99%

**Table C-2. Container Residue Processing Method**

Product	Associated Processing Methods	Recommended ESD Default Release Media
CVD Gases	Cylinders are not typically cleaned. Recovered gas is: <ul style="list-style-type: none"> <li>• Returned to commercial use;</li> <li>• Sold for another use;</li> <li>• Sent for waste water treatment;</li> <li>• Deep well injected; or</li> <li>• Incinerated.</li> </ul>	Wastewater treatment, deep well injection or incineration
CVD Liquids	Recovered precursor and spent cleaning agent containing residual CVD material is either: <ul style="list-style-type: none"> <li>• Returned to commercial use;</li> <li>• Discharged to sewer/POTW (via cleaning water);</li> <li>• Incinerated (solvents);</li> <li>• Vented to carbon absorber, which is managed as a non-hazardous waste (hot nitrogen); or</li> <li>• Dilute mixed acid is precipitated and the precipitated material is landfilled.</li> </ul>	POTW, incineration or landfill
CVD Solids <sup>a</sup>	Recovered precursor and spent cleaning agent containing residual CVD material is: <ul style="list-style-type: none"> <li>• Returned to commercial use;</li> <li>• Discharged to sewer/POTW; or</li> <li>• Incinerated.</li> </ul>	POTW or incineration

Note: Information on container cleaning and waste disposal method based on one major specialty chemicals manufacturer in the industry (Industry, 2009). According to this company, transport containers are reused and not disposed.

<sup>a</sup>This table provides available information on the method for cleaning and disposing containers used to transport solid precursors. However, most precursors are expected to be in the form of either a gas or a liquid. This ESD does not address releases of and exposures to solid precursors.

<sup>b</sup> Gas cylinders are typically only cleaned upon initial use or if change service or disposal is required. The company providing this information did not specify how often the containers are replaced and disposed.

EPA suggests that a 16-gallon (approximately 60.6 liters) container be used as a default transport container in the absence of site-specific information (see Section 3.7).

If the number of containers used per site per year ( $N_{\text{container\_unload\_site\_yr}}$ ) is fewer than the days of operation at the supplier site, the days of release equals the number of containers and the daily release is calculated based on the following equation:

$$E_{\text{local\_container\_residue\_disp}} = V_{\text{container}} \times \rho_{\text{formulation}} \times F_{\text{chem}} \times F_{\text{container\_disp}} \times 1 \frac{\text{container}}{\text{site} \cdot \text{day}} \quad (\text{C-1a})$$

This release will occur over  $[N_{\text{container\_unload\_site\_yr}}]$  days/year from  $[N_{\text{sites}}]$  sites. Note the release occurs at the *chemical supplier site* and the number of site ( $N_{\text{sites}}$ ) differs from that estimated in the body this ESD.

Where:

$E_{\text{local\_container\_residue\_disp}}$	=	Daily release of chemical from container residue (kg chemical/site-day)
$V_{\text{container}}$	=	Volume of transport container (Default: 16 gallon or 60.6 L chemical/container (for a small container))
$\rho_{\text{formulation}}$	=	Density of chemical formulation (kg/L formulation); (Default: 1 kg/L for liquid; 0.52 kg/L for pressurized gas <sup>21</sup> )
$F_{\text{chem}}$	=	Weight fraction of the chemical in formulation (Default: 1 kg precursor chemical/kg formulation)
$F_{\text{container\_disp}}$	=	Fraction of chemical remaining in the container as residue (Default: 0.1 kg container residue/kg formulation)

If the number of containers used per site per year ( $N_{\text{container\_unload\_site\_yr}}$ ) is greater than the days of operation, the days of release equal the days of operation, and the average daily release is calculated based on Equation C-1b. Note this may also be used if a container size is not assumed in Equation C-1a and the number of containers used per site-year is unknown.

$$E_{\text{local\_container\_residue\_disp}} = Q_{\text{chem\_site\_day}} \times F_{\text{container\_disp}} \quad (\text{C-1b})$$

This release will occur over  $[\text{TIME}_{\text{operating\_days}}]$  days/year from  $[N_{\text{sites}}]$  sites. Note the release occurs at the *chemical supplier site* and the number of operating days ( $\text{TIME}_{\text{operating\_days}}$ ) and the number of site ( $N_{\text{sites}}$ ) differ from those estimated in this ESD.

<sup>21</sup> Default values based on the density of water and compressed trimethylsilane (Air Products, 2006). See Appendix B for alternate values for compressed gases.

Where:

$$\begin{aligned}
 E_{\text{local\_container\_residue\_disp}} &= \text{Daily release of chemical from container residue (kg chemical/site-day)} \\
 Q_{\text{chem\_site\_day}} &= \text{Daily use rate of chemical precursor (kg chemical/site-day)} \\
 F_{\text{container\_disp}} &= \text{Fraction of chemical remaining in the container as residue (Default: 0.1 kg container residue/kg formulation)}
 \end{aligned}$$

No information is available on the number of operating days per year at the supplier site. CEB typically assumes that most industrial facilities operate 250 days per year, based on a five-day workweek and a two-week operation shut down for maintenance and holidays (CEB, 1991).

As default, release from container cleaning should be assessed to wastewater treatment (e.g. public owned treatment works (POTW)), incineration, or landfill (potentially precipitated material). This approach conservatively assumes all of the container residues are disposed. Site-specific information on reuse and recycle should be evaluated, when available, when assessing the release. Further, Table C-1 should be referred to determine the specific waste disposal method and the receiving environmental media when the physical form of the CVD precursor is known. The estimated release quantity does not differ for liquids and gases based on the method presented in this ESD.

EPA notes the use of chemical- or site-specific information should supersede generic data presented in Table C-1 and Table C-2, when available.

### Release to Air from Container Cleaning

Many CVD precursors are volatile liquids or gases. Due to reasons of volatility and worker safety, CVD containers are likely cleaned using custom designed equipment inside a contained space (Industry, 2009) if the chemical is highly volatile, toxic, or pyrophoric. Therefore, volatilization would be mitigated through engineering controls for these chemicals. Volatile releases to air are also expected to be negligible for chemicals with low vapour pressure (vapour pressure < 0.001 torr) – regardless of the type of control equipment implemented.

For semi-volatile liquids (vapour pressures between 0.001 torr and 35 torr) and for highly volatile liquids (vapour pressures above 35 torr), no industry-specific monitoring data or EPA models are currently available to estimate releases. As such, this ESD recommends using monitoring data for analogous chemicals or processes to estimate the airborne concentration of vapours associated with this activity. In each case, similarities must exist in physical/chemical properties of the chemicals, nature of workplace environment, quantities of material handled, and work activities associated with use of the chemical. The following simple relationship has been derived to estimate airborne concentrations for vapours from analogous data:

$$C_{v,\text{chem}} = C_{v,k} \times \frac{VP_{\text{chem}} \cdot x_{\text{chem}}}{VP_k \cdot x_k} \quad (\text{C-2})$$

Where:

$C_{v, \text{chem}}$	= Estimated airborne concentration of chemical precursor (ppm)
$C_{v, k}$	= Estimated airborne concentration of the known chemical (ppm) (Default: see Table C-3)
$VP_{\text{chem}}$	= Vapour pressure of the chemical precursor (torr)
$VP_k$	= Vapour pressure of the known chemical (torr)
$X_{\text{chem}}$	= Mole fraction of the chemical precursor (dimensionless)
$X_k$	= Mole fraction of the known chemical (dimensionless)

Table C-3 provides some suggested values for  $C_{v, k}$  based on personal monitoring of HCFC-22, extracted from the *Occupational Exposure and Environmental Release Data for Chlorofluorocarbons (CFCs) and Their Substitutes* (EPA, 1990). As conservative, this ESD recommends the use of 90<sup>th</sup> percentile airborne concentration of HCFC-22 as analogous data. These data should only be used in the absence of relevant data or when the PMN submission does not include air abatement information.

**Table C-3. HCFC-22 Monitoring Data related to Container Handling Activities during HCFC Manufacturing**

Job Title	Sample Duration (min)	Concentration (ppm)
Cyl Pkgr Op	292	0.15
Cyl Pkgr Op	281	0.11
Ton Cyl Pkgr Op	282	0.1
Tk Car Loader	275	0.05
Cyl Loader	370	10.95
Cyl Loader	216	0.7
Ton Cyl Loader	173	0.01
<b>90<sup>th</sup> Percentile (Default)</b>		<b>4.8</b>
Note: HCFC-22 Molecular Weight: 86.5 g/mol HCFC-22 vapour pressure: 7,846 torr		

Source: EPA, 1990.

The following equations can subsequently be used to estimate air releases ( $E_{\text{local,air\_cleaning}}$ ) from highly-volatile chemicals during container cleaning (EPA, 2011). The equations assume the air generation rate for the chemical precursor reaches steady-state, and that  $C_{v, \text{chem}}$  is representative of the near-field airborne concentration at steady-state.

$$Q_{\text{NF}} = 0.984 \times \text{FSA} \times v_{\text{NF}} \quad (\text{C-3})$$

$$G_{\text{air}} = 1.93\text{E}-11 \times \left( 1 - \frac{Q_{\text{NF}}}{Q_{\text{NF}} + Q_{\text{FF}}} \right) \times C_{v, \text{chem}} \times Q_{\text{NF}} \times \text{MW}_{\text{chem}} \quad (\text{C-4})$$

$$E_{\text{local,air\_cleaning}} = G_{\text{air}} \times \frac{3600\text{s}}{\text{hr}} \times \text{TIME}_{\text{activity\_hurs}} \quad (\text{C-5})$$

Where:

$E_{\text{local\_air\_cleaning}}$	=	Daily release of chemical from container cleaning (kg chemical/site-day)
$G_{\text{air}}$	=	Generation rate of chemical precursor (kg chemical/s)
$Q_{\text{NF}}$	=	Near-field ventilation rate (ft <sup>3</sup> /min)
$Q_{\text{FF}}$	=	Far-field ventilation rate (ft <sup>3</sup> /min) (Default: 3,000 ft <sup>3</sup> /min; CEB, 1991)
FSA	=	Free surface area (ft <sup>2</sup> ) (Default: 81 ft <sup>2</sup> ; see EPA, 2011 <sup>22</sup> )
$MW_{\text{chem}}$	=	Molecular weight of the chemical precursor (g/mol)
$V_{\text{NF}}$	=	Near-field air speed (cm/s) (Default: 30 cm/s; see EPA, 2011)
$TIME_{\text{activity\_hours}}$	=	Operating hours for the activity (hr/site-day), equals to the number of containers per site-day <sup>23</sup> divided by the unload/fill rate <sup>24</sup> , see CEB, 2002 for reference to this approach. (Default for unload/fill rate: 60 containers/hr for small containers; ChemSTEER, 2005)

See *Generic Model to Estimate Air Releases from Airborne Concentrations* (EPA, 2011) for additional information on the derivation of the equations and recommended default values.

This release will occur over the lesser of [ $N_{\text{container\_unload\_site\_yr}}$ ] or [ $TIME_{\text{operating}}$ ] days/year from [ $N_{\text{sites}}$ ] sites. The release should be assessed at the *chemical supplier site* and not at the end use site. Depending on the facility, engineering controls may be in place to prevent direct releases of these chemicals to air.

EPA notes the use of chemical- or site-specific data should supersede generic model presented above. In addition, EPA recommends that users of this ESD reference PMN submission to determine air abatement deployed for a specific precursor.

### Sample Calculations for Release to Wastewater Treatment, Incineration, or Landfill from Container Residue

The following is a sample calculation using Equation C-1a, which assumes the number of containers used per site per year is fewer than the days of operation at the supplier site:

$$E_{\text{local\_container\_residue\_disp}} = V_{\text{container}} \times \rho_{\text{formulation}} \times F_{\text{chem}} \times F_{\text{container\_disp}} \times 1 \frac{\text{container}}{\text{site} \cdot \text{day}}$$

<sup>22</sup> CEB Generic Model to Estimate Air Releases from Airborne Concentrations, EPA, 2011 (unpublished).

<sup>23</sup> This is the number of containers unloaded at the supplier site. It is assumed that this value equals the total number of containers unloaded at all end use sites (see Section 4.3).

<sup>24</sup> The CEB, 2002 reference provides an approach for using the default fill rate and the amount of material loaded into/unloaded from containers to determine the hours for this activity.

$$\begin{aligned} \text{Elocal}_{\text{container\_residue\_dsp}} &= \frac{60.6 \text{ L formulation}}{\text{container}} \times \frac{1 \text{ kg}}{\text{L}} \times 1.0 \times \frac{0.1 \text{ kg disposed}}{\text{kg formulation}} \times \frac{1 \text{ container}}{\text{site} \cdot \text{day}} \\ \text{Elocal}_{\text{container\_residue\_dsp}} &= 6.06 \frac{\text{kg chemical disposed}}{\text{site} \cdot \text{day}} \end{aligned}$$

The days of release will equal the number of containers unloaded at the site. Because transport containers are returned to the chemical manufacturers for cleaning and refilling, the release will occur at the manufacturer (supplier) site.

Media of release: water (wastewater treatment or POTW), incineration, or landfill (see Table C-1 for liquids)

### Sample Calculation for Release to Air from Volatile Precursor during Container Cleaning

*For semi-volatile and highly volatile liquids:*

For the purpose of this calculation, the chemical precursor is assumed to have a vapour pressure of 2,000 torr and a mole fraction of 1.

$$C_{v, \text{chem}} = C_{v, k} \times \frac{\text{VP}_{\text{chem}} \cdot x_{\text{chem}}}{\text{VP}_k \cdot x_k} = 4.8 \text{ ppm} \times \frac{2,000 \text{ torr} \cdot 1}{7,846 \text{ torr} \cdot 1} = 1.22 \text{ ppm} \quad (\text{C-2})$$

2)

$$Q_{\text{NF}} = 0.984 \times \text{FSA} \times v_{\text{NF}} = 0.984 \times 81 \text{ ft}^2 \times 30 \frac{\text{cm}}{\text{s}} = 2,391 \frac{\text{ft}^3}{\text{min}} \quad (\text{C-3})$$

$$G_{\text{air}} = 1.93\text{E}-11 \times \left( 1 - \frac{Q_{\text{NF}}}{Q_{\text{NF}} + Q_{\text{FF}}} \right) \times C_{v, \text{chem}} \times Q_{\text{NF}} \times \text{MW}_{\text{chem}} \quad (\text{C-4})$$

$$G_{\text{air}} = 1.93\text{E}-11 \times \left( 1 - \frac{2,391}{2,391 + 3,000} \right) \times 1.22 \times 2,391 \times 100 = 3.13\text{E}-6 \frac{\text{kg}}{\text{s}}$$

$$\text{Elocal}_{\text{air\_cleaning}} = G_{\text{air}} \times \frac{3600 \text{ s}}{\text{hr}} \times \text{TIME}_{\text{activity\_hours}} \quad (\text{C-5})$$

$$\text{Elocal}_{\text{air\_cleaning}} = 3.13\text{E}-6 \frac{\text{kg}}{\text{s}} \times \frac{3600 \text{ s}}{\text{hr}} \times \frac{1 \text{ containers/site} \cdot \text{day}}{60 \text{ containers/hr}} = 1.88\text{E}-4 \frac{\text{kg}}{\text{site} \cdot \text{day}}$$

Media of release: air

**APPENDIX D**

**OCCUPATIONAL EXPOSURES AT THE CHEMICAL SUPPLIER SITE**

## Number of Workers at the Chemical Supplier Site

Workers at the chemical supplier site are potentially exposed to CVD precursors while handling empty containers returned from the end users. Information on the number of workers is typically found in PMN submissions. A search of past PMN cases submitted to EPA between 2006 and 2010 indicates the number of workers at these sites involved in container handling and cleaning activities ranges from one to four. When chemical-specific information is not available, this ESD assumes *up to 4 workers per site* could be exposed to CVD precursors during container cleaning activities.

## Dermal and Inhalation Exposure during Container Cleaning

CVD precursors are shipped to semiconductor manufacturing facilities for use. Once emptied, containers are shipped back to the supplier for cleaning and/or refilling. Because of concerns for worker safety and process contamination, engineering controls are likely in place to prevent leakage and subsequent exposure at the supplier site. Specialty chemical suppliers stated that all activities associated with container handling (e.g. filling, connecting, and cleaning) are conducted inside a glove box or in other ventilated and enclosed environments with local area monitoring and alarms to indicate a release (Industry, 2013). For bulk chemical containers, the connection points (rather than the entire container) are contained and ventilated. For liquid CVD precursors, the containers are first moved inside a glove box or containment with an inert atmosphere and the residual chemical is flushed from the container. Then, the container is attached to another custom built processing station where the container interior is washed with three different solvents. Finally, trace particles remaining in the container are removed using an ultrasonic bath. The final processing occurs inside a Class 100 clean room (Industry, 2009).

Workers are likely to be physically separated from the chemical of interest during container cleaning activities. When possible, chemical handling facilities are designed as closed systems with no worker exposure. When exposure cannot be eliminated, worker exposures are minimized by the use of engineering control and PPE. Container handling procedures and typical RMM are listed in Table C-1. When information is available, EPA recommends users of this ESD to reference PMN submissions to address the potential for exposure at chemical manufacturer sites.

### ***Inhalation Exposure:***

Inhalation exposure is assumed to be negligible for chemicals with vapour pressures below 0.001 torr. Inhalation exposure is assumed to be mitigated through engineering controls for chemicals that are toxic, reactive or pyrophoric.

For chemicals that are semi-volatile (vapour pressures between 0.001 torr and 35 torr) and highly volatile (vapour pressures above 35 torr), EPA recommends the use of analogous data to estimate the airborne concentration of the chemical precursor (see Appendix D). Table C-3 presents analogous data from the CFC study, which contains measured exposure values related to container handling operations for HCFC-22. The HCFC-22 exposure ranged from 0.01 to 10.95 ppm, with a 90<sup>th</sup> percentile exposure of 4.8 ppm (EPA, 1990).

The following equation can then be applied to estimate inhalation exposure to the assessed chemical of interest:

$$EXP_{\text{inhalation}} = C_{\text{v, chem}} \times \frac{MW_{\text{chem}}}{V_{\text{molar}}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \quad (\text{D-1})$$

Where:

- $EXP_{\text{inhalation}}$  = Potential inhalation exposure to the CVD precursor per day (mg chemical/day)
- $C_{\text{v, chem}}$  = Estimated airborne concentration of chemical precursor (ppm) (see Equation D-2)
- $MW_{\text{chem}}$  = Molecular weight of the CVD precursor (g/mol)
- $V_{\text{molar}}$  = Molar volume of the CVD precursor (Default: 24.45 L/mol at 25°C, based on ideal gas assumption)
- $RATE_{\text{breathing}}$  = Inhalation rate (Default: 1.25 m<sup>3</sup>/hr) (CEB, 1991)
- $TIME_{\text{exposure}}$  = Exposure duration (Default: 8 hr/day)

This exposure will occur over the lesser of  $N_{\text{container\_unload\_site\_yr}}$  or  $TIME_{\text{operating\_days}}$  (consistent with Appendix C).

### ***Dermal Exposure:***

The CEB Engineering Manual (CEB, 1991) describes EPA's guidelines for assessing dermal exposure to gases and vapours. For these materials, a quantitative estimate should not be made. Rather, qualitative estimates should be used to describe dermal exposure using one of the following exposure categories: 1) None; 2) Very low; 3) Incidental contact; 4) Intermittent contact; 5) Routine contact; or 6) Routine immersion. It should be acknowledged that some dermal contact will occur in the absence of protective clothing (See CEB Engineering Manual, Section IV. Modeling Workplace Exposure). Note any chemical with very high volatility will evaporate almost instantaneously from the skin, and the rapid evaporation suggests that skin absorption is negligible (Patty's, 1987).

### **Sample Calculation for Dermal and Inhalation Exposure to CVD Precursor during Container Cleaning**

#### ***Inhalation (semi-volatile and highly volatile)***

Inhalation exposure to semi-volatile and highly volatile liquids during container cleaning can be calculated using the following equation:

$$EXP_{\text{inhalation}} = C_{\text{v, chem}} \times \frac{MW_{\text{chem}}}{V_{\text{molar}}} \times RATE_{\text{breathing}} \times TIME_{\text{exposure}} \quad (\text{D-1})$$

$$EXP_{\text{inhalation}} = 1.22 \text{ ppm} \times \frac{100 \text{ g/mol}}{24.45 \text{ L/mol}} \times 1.25 \frac{\text{m}}{\text{hr}} \times 0.016 \frac{\text{hr}}{\text{day}} = 0.1 \frac{\text{mg}}{\text{day}}$$

Up to 4 workers per site will be exposed.

**APPENDIX E**

**WORKER MONITORING DATA AT SEMICONDUCTOR FABs**

Table E-1. Worker Monitoring Data for CVD Operations

Worker Activity	Number of Workers*	Precursor Used/ Monitored	Surrogate Monitored (if any)	Typical Risk Management Measures	Measured Concentration	Sampling Duration (minutes)	Detection Limits	Monitoring Method	Monitoring Year / Location	
CVD vacuum system and exhaust maintenance.	15	Ammonia		Chemical resistant gloves, resistant chemical suit, respirator.	< 0.38 ppm	170	0.38 ppm	A	2012	Asia
CVD vacuum system and exhaust maintenance.	15	Ammonia		Chemical resistant gloves, resistant chemical suit, respirator.	< 0.37 ppm	170	0.37 ppm	A	2012	Asia
CVD equipment maintenance.	20	Ammonia		Airline respirator	<0.30 ppm	15	0.30 ppm	A	2012	Asia
CVD equipment maintenance.	20	Ammonia		Airline respirator	<0.26 ppm	15	0.26 ppm	A	2012	Asia
CVD equipment maintenance.	20	Ammonia		Airline respirator	<0.26 ppm	15	0.26 ppm	A	2012	Asia
CVD equipment maintenance.	20	Ammonia		Air Purifying Respirator	<0.6 ppm	145	0.6 ppm	A	2012	Asia
CVD equipment maintenance.	20	Ammonia		Air Purifying Respirator	<0.5 ppm	145	0.5 ppm	A	2012	Asia
CVD equipment maintenance.	20	Nitrous Oxide		Air Purifying Respirator	<1.0 ppm	10	1 ppm	B	2012	Asia
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.1 ppm	81	0.1 ppm	A	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	chlorine		<0.02 ppm	83	0.02 ppm	A	2012	North America

Worker Activity	Number of Workers*	Precursor Used/ Monitored	Surrogate Monitored (if any)	Typical Risk Management Measures	Measured Concentration	Sampling Duration (minutes)	Detection Limits	Monitoring Method	Monitoring Year / Location	
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.1 ppm	81	0.1 ppm	A	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.3 ppm	57	0.3 ppm	B	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.05 ppm	323	0.05 ppm	B	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.2 ppm	70	0.2 ppm	B	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.3 ppm	60	0.3 ppm	B	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.05 ppm	333	0.05 ppm	B	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.3 ppm	333	0.3 ppm	B	2012	North America
CVD equipment maintenance.		dichlorosilane, HCl	HCl		<0.08 ppm	212	0.08 ppm	B	2012	North America
CVD equipment maintenance.		NH3			<1.2 ppm	205	1.2 ppm	A	2012	North America
CVD equipment maintenance.		HCl, dichlorosilane	HCl		<0.03 ppm	205	0.03 ppm	A	2012	North America
CVD equipment maintenance.		dichlorosilane	Cl2		<0.008 ppm	205	0.008 ppm	A	2012	North America
CVD equipment maintenance.		diborane	boron		<0.0037 ppm	205	0.0037 ppm	A	2012	North America
Other task		TEOS	particulate		<0.51 mg/m3	99	0.51 mg/m3	A	2012	North America

Worker Activity	Number of Workers*	Precursor Used/ Monitored	Surrogate Monitored (if any)	Typical Risk Management Measures	Measured Concentration	Sampling Duration (minutes)	Detection Limits	Monitoring Method	Monitoring Year / Location	
Other task		TEOS	particulate		<0.51 mg/m <sup>3</sup>	99	0.51 mg/m <sup>3</sup>	B	2012	North America

Source: Industry, 2014.

Monitoring Method A - Air concentration measurements from personal sampling pumps Monitoring Method B – Other

\*Maximum number of employees per fab associated with each activity (total for all shifts) “-“ No data available / provide