SIA Comments
On the
Draft Scope of the Risk Evaluation for trans-1,2-Dichloroethylene

EPA-HQ-OPPT-2018-0465

CASRN 156-60-5

Submitted May 26, 2020

The Semiconductor Industry Association (SIA) submits these comments to the U.S. Environmental Protection Agency (EPA) on the Draft Scope of the Risk Evaluation for trans-1,2-dichloroethylene (CASRN 156-60-5).

SIA is the trade association representing leading U.S. companies engaged in the design and manufacture of semiconductors. Semiconductors are the fundamental enabling technology of modern electronics that has transformed virtually all aspects of our economy, ranging from information technology, telecommunications, health care, transportation, energy, and national defense. The U.S. is the global leader in the semiconductor industry, and continued U.S. leadership in semiconductor technology is essential to America's continued global economic leadership. More information about SIA and the semiconductor industry is available at www.semiconductors.org.

This document provides a summary of our industry's manufacturing process, our uses of trans-1,2-dichloroethylene, and information on the conditions of use relevant to EPA's scoping exercise.

I. Background on Semiconductor Manufacturing

A. Overview of the Semiconductor Manufacturing Process

Semiconductor device fabrication is the process used to create integrated circuits that are present in electrical and electronic devices. An overview of semiconductor manufacturing process can be found in OECD emissions scenario documents.[1] The fabrication process (see Figure 1) begins with a wafer of semiconductor material varying in size from 150-300mm in diameter and includes a sequence of photographic and chemical processing steps during which electronic circuits are gradually created on the wafer substrate. These electrical circuits are made one layer at a time by the combination of putting a layer on the surface of the wafer and using a patterning process to then remove designated parts of the layer to leave behind a specific shape. Advanced semiconductors may contain billions of transistors on a layer of silicon the size of a square centimeter, so manufacturing must be rigorously controlled and conducted with great precision to achieve features at the nanoscale. The basic steps of semiconductor manufacturing include:

- Oxidation, a process usually performed at 800-1200 degrees C in a tube furnace, is a batch process that diffuses oxygen (O_2) or water (H_2O) vapor into the silicon wafer to

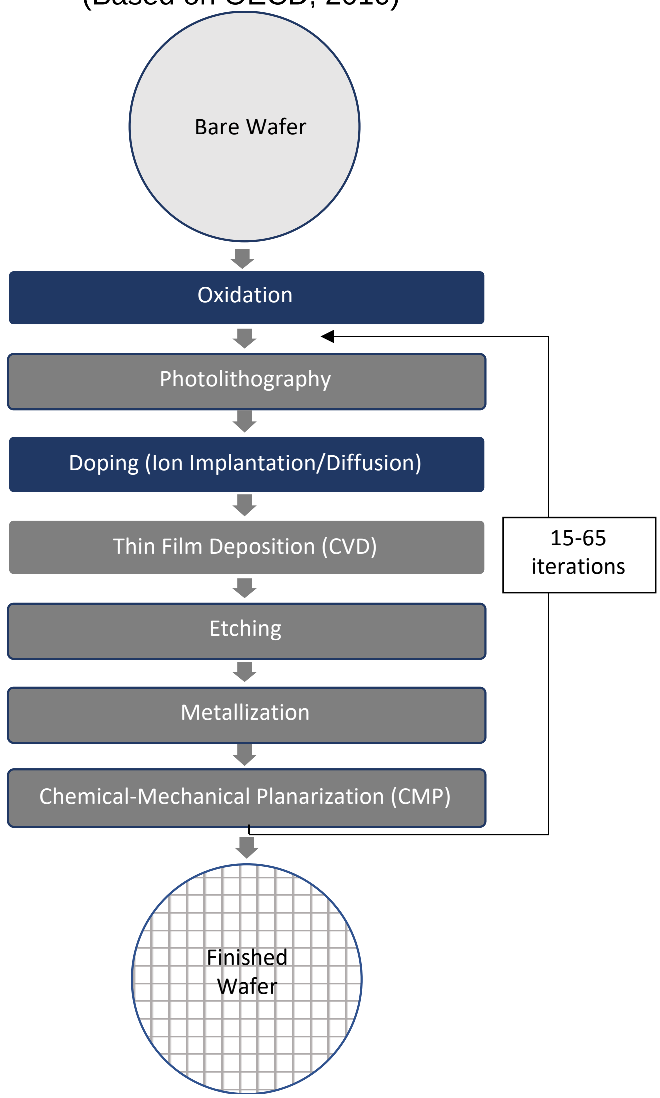
[1] ENV/JM/MONO(2015)5; ENV/JM/MONO(2004)14/REV1.

form a silicon dioxide (SiO_2) layer that protects the wafer surface during subsequent steps. Trans-1,2-dichloroethylene is used in the oxidation step as a source of Chlorine (Cl_2) to sequester metals that can contaminate the wafer and as a source of H_2O. It is also used to clean furnace tubes.

- During the photolithography step, the wafer is coated with a layer of photoresist and subsequently covered with a mask that defines the specific patterns to be retained or removed in subsequent processes. In a typical processing scheme, the photoresist polymer formulation is applied to a spinning wafer, and then subjected to a pre-exposure bake to drive off a proportion of the solvent to impart dimensional stability to the film.
- The coated wafer substrate is then exposed thru a patterned photomask, with actinic radiation from a light source of specified wavelength. Reflectivity of the semiconductor material during light exposure can be problematic. To absorb light and reduce reflections during the exposure, a layer of anti-reflective coating is typically utilized. An anti-reflective coating applied after the photoresist is referred to as a top antireflective coating (TARC) agent and an anti-reflective coating applied before the photoresist is referred to as a bottom anti-reflective coating (BARC) layer.
- After exposure, the coated wafer substrate undergoes a development process whereby the previously exposed regions are selectively dissolved and removed from the photoresist film. This leaves the wafer surface with a patterned coating of photoresist, where in selected regions the resist material is completely removed, and where in the remaining areas the photoresist forms a protective coating. The open areas of the substrate may then be subjected to additive processes like physical vapor deposition, chemical vapor deposition, diffusion, ion implant or plating; or subtractive process like a plasma etch.
- In deposition, thin layers or films are added to the wafer surface to change its electrical properties or to serve as masks.
- In etching, specific areas of a deposited film are chemically removed so that an underlying material is exposed or another material may be deposited. Etching may be performed in a wet process using solutions of acids, bases or oxidizers, or in a dry process using various gases in a plasma.
- In Doping/Diffusion, atoms with one less electron than silicon (such as boron) or one more electron than silicon (such as phosphorus) are introduced into the area exposed by the etch process, to alter the electrical character (conductivity) of the silicon. Diffusion is a high temperature batch process in which wafers are loaded into a quartz tube where impurities are added to change the conductivity of the surface layer. Trans-1,2-dichloroethylene is used as a source of Cl_2 to sequester metals that can contaminate the wafer and as a source of H_2O. It is also used to clean furnace tubes.
- Subsequent to the etch or deposition process, the residual photoresist and anti-reflective coating must be removed from the wafer surface. This final step, known as the photoresist strip step, must be accomplished in a manner that completely and uniformly removes the residual photoresist, without adversely impacting the surfaces of the materials comprising the underlying wafer substrate (Dean et al, 1992; Lee et al, 1994).
- Cleaning occurs in various parts of the process flow and is also an important part of the wafer fabrication process as semiconductor devices are highly susceptible to various kinds of contamination such as particles, metal ions, chemicals, bacteria, and airborne molecular contaminants.
- Dielectric Deposition and Metallization - Following completion of the "front end," the individual devices are interconnected using a series of alternating metal depositions and dielectric films, with their respective patterning.

- Passivation- After the last metal is patterned, a final insulating layer (passivation) is deposited to protect the circuit from damage and contamination. Openings are etched in this film to allow access to the top metal later by electrical probes and subsequent wire bonds.
- Assembly and Packaging - A diamond saw slices the wafer into single chips. Sizes can vary from 1 x 1 mm to 76 x 56mm. Each chip is then assembled into an appropriate package that provides the contact leads for the chip. In one type of interconnect a wire bonding machine attaches wires, a fraction of the width of a human hair, to the leads of the package.

Figure 1: Overall Process Flow Diagram – Semiconductor Manufacturing[2]
(Blue boxes signify steps where trans-1,2-dichloroethylene may be)
(Based on OECD, 2010)



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

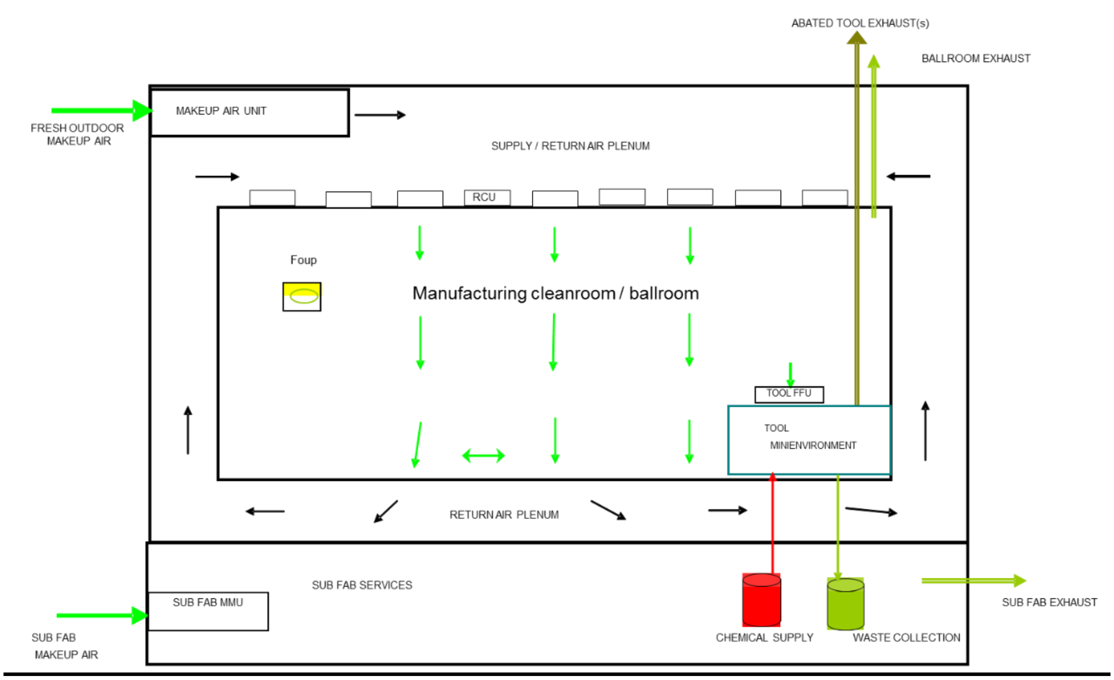
B. Semiconductor Manufacturing – Fab Cleanrooms and Equipment

The fabrication of semiconductors is conducted in specialized buildings known as “fabs” that involve the use of cleanrooms, and a hierarchy of design features that isolate workers and wafers from chemicals. The fab cleanroom design approach protects manufacturing personnel and is also critical to semiconductor wafer product quality. Figure 2 illustrates schematically the design of a typical 300mm fab. The fab consists of a cleanroom where the manufacturing operations are conducted, and an isolated ancillary space which contains chemical and air handling equipment, emission controls, and other infrastructure, and which is often located in an area within the building known as a “sub-fab”.

The fabrication of an integrated circuit on a silicon wafer involves a sequence of hundreds of additive, subtractive, photolithography, and cleaning steps that is accomplished by shuttling wafers between specialized manufacturing “tools” within which the individual unit operations are conducted on the wafer. The manufacturing tools, engineers and operators are located within the cleanroom, but the tools are supplied with chemicals, power, and other utility services from the subfab or other ancillary space.

As also indicated on Figure 2, fresh air is brought into the fab thru an air conditioning unit that controls the fab air temperature and humidity, and is recirculated through ultra-low particulate air (ULPA) filters before being exhausted to the building exterior. In a typical 300mm wafer manufacturing fab built in 2000, the entire volume of air in the fab cleanroom is replaced every 7 minutes, and the entire volume of air in the cleanroom is recirculated through the ULPA filters at a rate of once every 0.64 minute. This extensive level of air circulation and replacement provides an exceptional level of fab air cleanliness.

Figure 2. Schematic of airflow in a typical Fab.



In all semiconductor manufacturing, regardless of the level of sophistication of the factory, equipment systems operate with intrinsic controls that minimize or eliminate chemical liquid or vapor exposure potential during normal equipment operations. The equipment must be maintained frequently, which requires the operating parts of the equipment to be placed in stand-by (non-operating mode) and the opening of protective enclosures. During these maintenance activities, workers utilize protective equipment to reduce the potential for employee exposure. Older manufacturing equipment (150mm and older) is generally less sophisticated with varying degrees of protective equipment controls. In those cases, more PPE is used to protect the employee during operations. Even in these cases a high degree of engineering controls are used to ensure employee exposure is minimized including exhaust, interlocks, and monitoring. In all cases where engineering controls are not available, administrative controls are used to minimize the potential for exposure.

During fabrication, the wafers are highly susceptible to even minute amounts of contamination, and so the wafers are moved in and out of tools by robotics, placed robotically into enclosed boxes, known as front opening unified pods (FOUPs), and shuttled between tools via a computer controlled, automated transport system. Figure 3, shows manufacturing tools aligned along one of many corridors within a typical 300mm fab, and Figure 4 an automated transport system that shuttles FOUPs between tools.

Figure 3. Photo of typical 300mm wafer manufacturing cleanroom.

Figure 4. Robotic system moves wafers inside enclosed containers (FOUPs).

II. Uses of trans-1,2-Dichloroethylene in the Semiconductor Industry

Overview of Semiconductor Uses of trans-1,2-Dichloroethylene

In the highly-controlled semiconductor manufacturing process, the semiconductor industry uses trans-1,2-dichloroethylene in the wafer fab as a liquid source material for the in-situ generation of high purity hydrogen chloride (HCl) or chlorine (Cl_2) for use in silicon oxidation in diffusion furnaces and in furnace tube cleaning. It also acts to sequester metal contaminants. Trans-1,2-dichloroethylene was developed as a replacement for TCA and TCE:

> *Liquid organic chlorides such as 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE) have been used to replace HCI in silicon oxidation and furnace tube cleaning. These liquid sources are easier to deliver and are less corrosive than HCI. Chlorine generated from HCI or liquid sources has historically been used to passivate ionic sodium, improve dielectric strength, and enhance minority carrier lifetimes as reviewed in Ref. 1. Properties of oxides grown with these sources have been studied extensively,24 and their use is widespread. However, TCE is a carcinogen and TCA has an ozone depletion potential (ODP) of 0.1.s*
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> *Alternative liquid sources first were identified based on their ODP, toxicity, and vapor pressure. Several of the more promising candidates were evaluated thermodynamically, and the list and selection criteria were*

further refined by kinetic studies. One exceptional candidate based on our results is trans-l,2-dichloro- ethylene (t-DCE).[3]

Trans-1,2-dichloroethylene is used in oxide furnaces operating at atmospheric pressure at a temperature range of 700-1200 deg C. The chemical is delivered as a liquid via nitrogen (N_2) push gas from a 20L quartz-lined stainless steel container in a bulk fill cabinet to refill a sealed quartz container with PVC coating in each tool. N_2 carrier gas is then bubbled through liquid in the quartz container to flow it into the furnace tube. Trans-1,2-dichloroethylene is fully transformed in the process into HCl and other inorganic chlorides.

$$C_2H_2Cl_2 + 2O_2 \longrightarrow 2HCl + 2\ CO_2$$

U.S. Patent 5288662[4] outlines two key results of processing trans-1,2-dichloroethylene to create the desired product, HCl. First the mass spectrometry chart, Figure 3 shows no trans-1,2-dichloroethylene residual. Second, as noted in section 5 of the patent residual trans-1,2-dichloroethylene in the process would, "contaminate the growing silicon oxide," which is the purpose of the process step. Further, Table VI shows at 800C the trans-1,2-dichloroethylene is non-detected relative to the desired products generated in the reaction chamber. Even the smallest concentration of trans-1,2-dichloroethylene left in the product would cause quality issues; these defects would render not only 1 chip defective but entire batches of wafers (75+) defective as typically the diffusion process is a batch process.

It is important to emphasize that no trans-1,2-dichloroethylene is left in the final product, which is a finished wafer that is then cut into individual semiconductor devices for assembly, packaging and test.

A. Importance of *trans*-1,2-dichloroethylene in Semiconductor Manufacturing

Halogens are important in silicon oxidation because they enhance the oxidation rate, increase resistance to gamma ray damage, and sequesters metal ions to ensure a clean Si-SiO_2 interface.[5] Trans-1,2-dichloroethylene provides a safer, non-ozone depleting source of HCl.

B. Absence of Safe Alternatives for Semiconductor Uses of *trans*-1,2-dichloroethylene

The semiconductor industry uses trans-1,2-dichloroethylene as a safer source of HCl and for improved process performance. 1,1,1-trichloroethane (TCA) was previously used as a source; however, due to concerns about the ozone depletion potential of TCA, trans-1,2-dichloroethylene was adopted in the early 1990s as a safer alternative.[6] HCl is an unacceptable substitute because of inferior process performance and the risk it poses to human health and the fab environment.

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[3] A. K. Hochberg *et al* 1992 *J. Electrochem. Soc.* **139** L117.

[4] Lagendijk, et al., 1994, *Low Ozone Depleting Chlorides for Use During Silicon Oxidation and Furnace Tube Cleaning*, US Patent 5288662.

[5] Doering, R., & Nishi, Y. (2017). *Handbook of semiconductor manufacturing technology, p.9-5*. CRC Press.

[6] Versum Materials Application Notes: Process Guidelines for Trans-LC.

III. Controls in Semiconductor Manufacturing

A. Controls Employed with Uses of trans-1,2-dichloroethylene

Use of trans-1,2-dichloroethylene in the semiconductor industry are subject to significant levels of control. Manufacturing tools are equipped with exhaust, interlocks to prevent an exposure during processing, a once-through closed path system, and pre-open cleaning procedures.

B. Containers, Storage and Delivery

Trans-1,2-dichloroethylene is supplied to the fab as a liquid in hermetically sealed 1.5L quartz source container with PVC coating and 20L quartz-lined stainless steel bulk container. The container is equipped with special valves featuring a locking nut-assembly and built-in quartz plunger which breaks the seal after the container has been installed into the tool and the valves opened. In addition to the valved inlet (w/ dip-tube) and outlet, there is a thermal-well designed into the container for temperature monitoring and a capped fill stem. The design of the chemical container results in no potential for exposure during installation or removal from the process tool.

Figure 5. trans-1,2-Dichloroethylene Source Container[7]

C. Waste Management and Controls

In normal semiconductor manufacturing use, trans-1,2-dichloroethylene is fully transformed in the process with no environmental release. Residual HCl and Cl_2 in the process effluent are sent to an acid exhaust system where they are abated via wet scrubber.

Empty containers are returned to the manufacturer for reprocessing and refilling.

[7] Source: Versum Materials, https://v8cnuz00-a.akamaihd.net/wp-content/uploads/2017/01/TransLC-w-1.pdf.

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D. Worker Exposure

Semiconductor fabs employ extensive and redundant controls to minimize the exposure of workers to chemicals of concern. The typical risk management measures and safety practices deployed at fabs to prevent trans-1,2-dichloroethylene releases and worker exposure include the following:

- Per the NIOSH hierarchy of controls, trans-1,2-dichloroethylene was adopted as a safer substitute for TCA, TCE and HCl gas.
- Fabs employ professional industrial hygienists that evaluate and control potential workplace exposures.
- Extensive engineering controls to prevent employee exposure.
- Extensive training in hazard communication, safe handling of chemicals, and proper use of personal protective equipment.
- Chemical storage, dispense and handling:
  - Segregated Storage per local codes
  - Automatic, ventilated, and fully enclosed supply and discharge systems
  - Personal protective equipment (PPE) worn during container change out (chemical resistant gown, chemical protective gloves, safety glasses/goggles, and face shield)
  - General ventilation and local exhaust ventilation
- Routine semiconductor manufacturing operations
  - Process tools are located in the clean room where a stringent clean regime is maintained as a requirement for production which also ensures no chemical releases
  - Closed systems
  - Continuous local exhaust ventilation under alarm
  - Automated chemical delivery (no chemical pouring)
- Invasive maintenance
  - Tool purged prior to invasive maintenance
  - Maintenance occurs at room temperature under local exhaust ventilation
  - Wearing of proper PPE as required.

Trans-1,2-dichloroethylene is used under highly controlled conditions and there is no expectation of worker exposure.

IV. Conclusion

The semiconductor industry uses trans-1,2-dichloroethylene with extensive controls for specialized uses to meet stringent performance requirements. Known alternatives pose significant increased risk to human health and the environment. As EPA continues its work on the scoping of trans-1,2-dichloroethylene and the future risk evaluation, we look forward to working closely with EPA to properly characterize the uses and potential risks in the semiconductor industry.