Updates to Environmental Release Estimates in the Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing

U.S. Environmental Protection Agency
Office of Pollution Prevention and Toxics
Chemical Engineering Branch
1200 Pennsylvania Avenue
Washington, D.C. 20460

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1.0 INTRODUCTION

This document provides updates to the environmental release estimates presented in the 2010 Organisation for Economic Co-operation and Development (OECD) Emission Scenario Document (ESD) on the Photoresist Use in Semiconductor Manufacturing. These revisions to the environmental release estimates presented in the 2010 ESD on Photoresist Use in Semiconductor Manufacturing are based on information provided by the Semiconductor Onium Photoacid Generator (PAG) Consortium. The Semiconductor Onium PAG Consortium developed a document titled *Semiconductor Photoacid Generator Use Rates and Releases,* which contains a conceptual model to estimate environmental releases [Semiconductor Onium PAG Consortium, 2017].

The updated environmental release estimates are presented in Section 4.0 of this document, followed by example calculations using these estimates in Section 6.0, and an example Initial Review Engineering Report (IRER) in Section 7.0, developed in EPA's Chemical Screening Tool for Exposures and Environmental Releases (ChemSTEER) software tool, using the original general facility estimates and the updated environmental release estimates for the 2010 ESD on Photoresist Use in Semiconductor Manufacturing.

1.1 Semiconductor Onium PAG Consortium Conceptual Model

The Semiconductor Onium PAG Consortium conceptual model is applicable to the use of onium PAGs at US semiconductor facilities. The document defines onium PAGs as: "Arylsulfonium compounds and their derivatives (such as triphenylsulfoniums and diphenylsulfoniums), aryliodoniums (such as diphenyliodoniums), and arylphosphoniums used as photo acid generators, thermal acid generators, and quenchers in organic formulations such as photoresists." The applicability of the information in this document to other photoacid generator components is uncertain.

Eight lithography chemical suppliers and 14 semiconductor manufacturing companies, operating 23 fabrication facilities, provided data to the Semiconductor Oniom PAG Consortium, which was used to develop the conceptual model. The chemical suppliers provided data to quantify the amount of onium salt (cation and anion) sold to the U.S. semiconductor industry in 2016. The semiconductor manufacturing companies provided information on wastewater discharge volumes and the publicly owned treatment works (POTWs) to which semiconductor manufacturers discharge.

1.2 Updates to Environmental Releases in the 2010 ESD on Photoresist Use in Semiconductor Manufacturing

The Semiconductor Onium PAG Consortium conceptual model contains updated release loss fractions and media of release information for certain release estimates provided in the 2010 ESD on Photoresist Use in Semiconductor Manufacturing. Semiconductor Onium PAG Consortium release estimates are summarized in Table 1-1, along with the changes that were made to the environmental release estimates of the 2010 ESD on the Photoresist Use in Semiconductor Manufacturing.

Table 1-1. Summary of Changes to the ESD

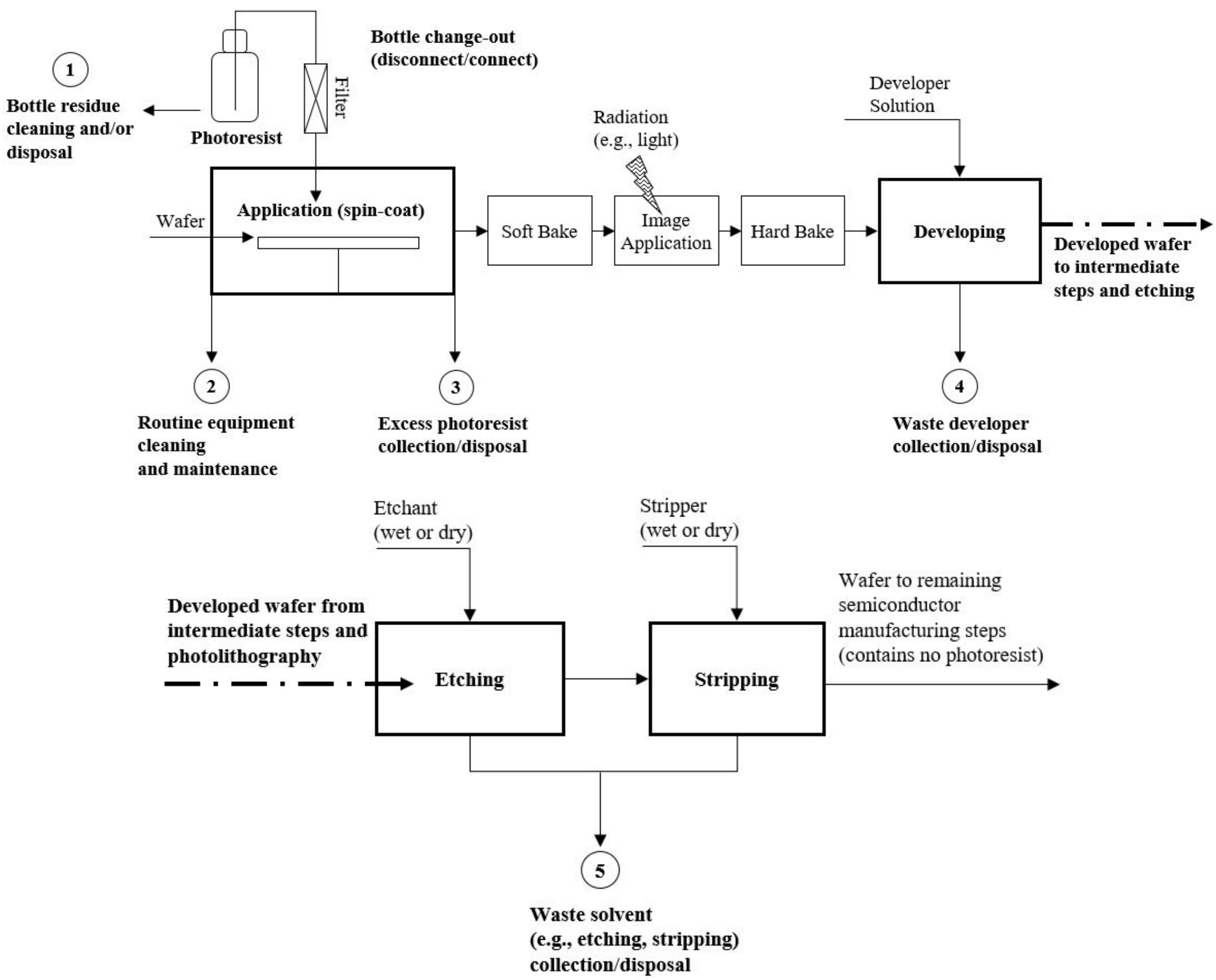
Release Source #	Description	2010 ESD Estimate	Semiconductor Onium PAG Consortium Estimate	Changes Made in this Document
1	Container residue	Loss Fraction: EPA/OPPT Small Container Residual Model, CEB standard 0.6% residual. Media of Release: Water, Incineration, or Landfill	Loss Fraction: No release estimate provided. Media of Release: Incineration	The media of release for this source was changed from uncertain to incineration.
2	Equipment cleaning and supply-line filter residues	Loss Fraction: EPA/OPPT Single Process Vessel Residual Model, CEB standard 1% residual. Media of Release: Incineration or Landfill	Loss Fraction: LF = 0.01. Media of Release: 50% to incineration, 50% to landfill	The information provided by the Semiconductor Onium PAG Consortium indicates release is to 50% incineration and 50% landfill, which is generally consistent with the 2010 ESD. No changes to the ESD were made; release media was left at incineration or landfill (without 50% split to each), to account for different equipment cleaning procedures.
3	Excess photoresist (spin-off)	Loss Fraction: Assumes 1-7% of the remaining photoresist (after releases 1 and 2) adheres to the wafer during application. The remaining 93% is spun-off and released. LF = (1 – 0.006 – 0.01) x (1 – 0.07) = 0.915. Media of Release: Incineration	Loss Fraction: Estimates 5.5% of applied photoresist adheres to wafer and remaining is spun-off and released. LF = (1 – 0.006 – 0.01) x (1-0.055) = 0.930. Media of Release: Incineration/ Fuel Blending	The estimate provided by the Semiconductor Onium PAG Consortium falls within the 1-7% presented in the ESD. No changes to the ESD were made, other than the addition of discussion regarding this estimate provided by the Consortium.
4	Residual photoresist contained in waste developer solution	Loss Fraction: Assumes 50% of adhered photoresist is released during the development process. LF = (1 – 0.006 – 0.01) x 0.07 x 0.5 = 0.0344. Media of Release: Water	Loss Fraction: Estimates 50% of adhered photoresist is released during the development process. LF = (1 – 0.006 – 0.01) x 0.055 x 0.5 = 0.0271. Media of Release: No information provided	The estimate provided by the Semiconductor Onium PAG Consortium agrees with that provided in the ESD. No changes were made to the ESD.

Table 1-1. Summary of Changes to the ESD

Release Source #	Description	2010 ESD Estimate	Semiconductor Onium PAG Consortium Estimate	Changes Made in this Document
5	Residual photoresist contained in waste etching and stripping solutions	<u>Loss Fraction</u>: Assume the remaining portion of the photoresist on the wafer that was not removed during developing is released during etching and stripping. LF = (1 – 0.006 – 0.01) x 0.07 x (1 – 0.5) = 0.0344. <u>Media of Release</u>: Water	<u>Loss Fraction</u>: Assumes the same overall release but breaks down this estimate into additional stages. LF = (1 – 0.006 – 0.01) x 0.055 x (1 – 0.5) = 0.0271. <u>Media of Release</u>: Water or Incineration	The media of release information was changed from water to water or incineration, based on the type of stripping process.

CEB = Chemical Engineering Branch (now the Risk Assessment Division [RAD])
OPPT = Office of Pollution Prevention and Toxics
LF = Loss Fraction

The updated release estimates based on the Semiconductor Onium PAG Consortium conceptual model are depicted in Figure 1 below. Note that this figure is identical to Figures 2-2a and 2-2b in the 2010 ESD on the Photoresist Use in Semiconductor Manufacturing, with updated environmental release media per Table 1-1.



Environmental Releases:

① Residue in empty photoresist transport containers (bottles) released to incineration.

② Equipment cleaning and routine maintenance (including supply line filter change-out) resulting in photoresist residues released to incineration or landfill.

③ Excess (spun-off) photoresist released to incineration.

④ Waste developer solvent containing residual photoresist released to on-site wastewater treatment.

⑤ Waste etching/stripping solvents containing residual photoresist released to on-site wastewater treatment or incineration. (In some cases, waste solvents may also be destroyed).

Figure 1. Release Points in the Photolithography Process from the 2010 ESD on Photoresist Use in Semiconductor Manufacturing

4.0 UPDATED ENVIRONMENTAL RELEASE ASSESSMENTS FROM THE 2010 ESD ON PHOTORESIST USE IN SEMICONDUCTOR MANUFACTURING

This section includes updated environmental release assessments from the 2010 ESD on Photoresist Use in Semiconductor Manufacturing. The original narrative and quantitative assessments from Section 4.0, “Environmental Release Assessments,” of the 2010 ESD are included in this section, with updates as specified in Table 1-1 of the previous section. Note that this section is numbered as Section 4, which is out of sequence from this document, to match the 2010 ESD on Photoresist Use in Semiconductor Manufacturing.

4.1 Background

This section presents approaches for calculating the amount of photoresist chemicals released form each release source as well as the most likely receiving media (i.e., air, water, landfill, incineration). The release sources are discussed in the order that they occur in the process (refer to Figure 1). The primary sources of releases include container residue, process equipment cleaning/supply-line filter residues, photoresist that does not adhere to the wafer in the application process, spent developer, and spent etching and stripping solutions. Table A-4 in Appendix A of the 2010 ESD lists key default values used for the release estimates, accompanied by their respective references.

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

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

Two of the environmental release estimates presented in this document are based on standard EPA release models. The remaining three estimates are based on information obtained from U.S. industry sources. Specifically, industry data was provided by the Semiconductor Oniom PAG Consortium and Semiconductor Industry Association (SIA) members. This data is comprised of information from eight lithography chemical suppliers and 14 semiconductor fabrication companies, which operate 23 fabrication facilities. This comprises about 9% of the estimated 268 semiconductor manufacturing facilities, per the estimate in Section 1.4 of the 2010 ESD. Table 4-1 summarizes the release estimation methods used in this ESD. Section 8 of the 2010 ESD presents a description of the sources reviewed and full citations for those specifically used in these calculations.

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

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

EPA has developed a software package (ChemSTEER) containing these models as well as all current EPA defaults. Appendix B of the 2010 ESD provides additional information on ChemSTEER, including instructions for obtaining the program, as well as background information, model equations, and default values for all standard EPA models.

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

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

OPPT – EPA's Office of Pollution Prevention and Toxics.
a – Appendix B of the 2010 ESD contains additional detailed descriptions for each of the models presented in this section.

4.2 Control Technologies

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

4.3 Container Residues Released to Incineration (Release 1)

Photoresist is typically supplied to the user in small containers, including one-liter or one-gallon (3.8-liter) bottles and one- to five-gallon (3.8 to 19-liter) NOW Pack bottles with a collapsible internal bladder [CEB, 1994a] [CEB, 2001b] [SIA, 2003]. Potential releases occur from cleanout and/or disposal of the used container. Container cleanout residues are disposed of with solvent waste via incineration, or the entire container is incinerated [Semiconductor Onium PAG Consortium, 2017]. In addition, industry practice is to incinerate NOW Pack internal bladders. Thus, EPA assumes that this release is to incineration.[1]

The amount of liquid photoresist remaining in the containers depends on the size of the container. Based on industry input from SIA, EPA suggests using a default container size of 1-gallon bottles in the absence of site-specific information; therefore, the *EPA/OPPT Small Container Residual Model* may be used to estimate this release. The model assumes that up to 0.6 percent of the liquid originally contained in small containers remains as residual after unloading [CEB, 1992]. The rationale, defaults, and limitations of this and alternative container residual models are further explained in Appendix B of the 2010 ESD.

The annual number of containers emptied ($N_{cont\_site\_yr}$) is estimated based on the average annual amount of photoresist received at each semiconductor manufacturing site and the container size (see Section 3.6 of the 2010 ESD). EPA recommends assuming 1-gallon (3.8-L) bottles and a density of 1 kg/L (density of water) as defaults, if chemical-specific information is unavailable. If the fraction of the chemical in the photoresist is unknown, assume 40 percent concentration, consistent with Section 3.4 of the 2010 ESD.

If the $N_{cont\_site\_yr}$ value is fewer than the days of application ($TIME_{apply\_days}$), the days of release equal $N_{cont\_site\_yr}$ (as calculated in Equation 3-4 of the 2010 ESD) and the daily release is calculated based on the following equation:

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

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

Where:

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

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

Q_{cont}	=	Mass of the photoresist in the container (kg photoresist/container) (default: use the same value used to estimate $N_{cont\_site\_yr}$ in Section 3.6 of the 2010 ESD)
F_{chem}	=	Mass fraction of the chemical of interest in the photoresist (kg chemical/kg photoresist) (see Section 3.4 of the 2010 ESD)
$F_{container\_disp}$	=	Mass fraction of photoresist remaining in the container as residue (default: 0.006 kg photoresist remaining/kg shipped for bottles [CEB, 1992]; see Appendix B of the 2010 ESD for defaults used for other container types)
$N_{cont\_site\_day}$	=	Number of containers emptied per site, per day (default: 1 container/site-day)

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

$$Elocal_{container\_residue\_disp} = Q_{chen\_received\_day} \times F_{container\_disp} \qquad \text{(Eqn. 4-1b)}$$

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

Where:

$Elocal_{container\_residue\_disp}$	=	Daily release of chemical of interest from container residue (kg chemical released/site-day)
$Q_{chem\_received\_day}$[2]	=	Daily amount of the chemical of interest received at the facility, prior to use/application (kg chemical received/site-day)
$F_{container\_disp}$	=	Mass fraction of photoresist remaining in the container as residue (default: 0.006 kg chemical remaining in container and released/kg received in full container, for bottles [CEB, 1992]; see Appendix B of the 2010 ESD for defaults used for other container types)

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

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

Where:

Q_{chem_day}	=	Daily use rate of the chemical of interest (kg chemical dispensed/site-day) (see Section 3.4 of the 2010 ESD)
$F_{container\_disp}$	=	Mass fraction of photoresist remaining in the container as residue (kg chemical remaining/kg received in full container) (see Section 4.3)

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

The amount of residual photoresist chemical remaining in the application equipment (e.g., spin-coat apparatus, supply line filter) may be estimated using the *EPA/OPPT Single Process Vessel Residual Model*. The model assumes that no more than one percent of the dispensed photoresist (i.e., the daily use rate of the chemical of interest, less the container residue) remains as residue that is released as equipment cleaning waste. Most facilities use various solvents to clean process equipment [ISESH, 2002]. Industry practices in Germany indicate these wastes are recycled or incinerated [UBA Germany, 2003]. U.S. industry information indicates that contaminated wipes from equipment cleaning are released to landfill, while solid equipment cleaning residues and cleaning solvents are treated as hazardous waste that is incinerated [Semiconductor Onium PAG Consortium, 2017]. Thus, EPA assumes equipment cleaning residues may be released to incineration or landfill [SIA, 2003].

One industry contact estimated that routine cleaning and maintenance activities may take place monthly or more frequently if the photoresist formulation is relatively thick/viscous (e.g., on a biweekly or weekly basis) and that supply line filters are changed out annually [Spinillo, 2005]. As a conservative estimate, daily equipment cleaning may be assumed (i.e., the days of release equal the days of application ($TIME_{apply\_days}$)), and the daily release of chemical residue in the process equipment is calculated using the following equation:

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

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

Where:

$Elocal_{equip\_disp}$	=	Daily release of chemical of interest from equipment cleaning (kg chemical released/site-day)
Q_{chem_day}	=	Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4 of the 2010 ESD)
F_{equip_disp}	=	Mass fraction of chemical released as residual in process equipment (default = 0.01 kg chemical released/kg chemical dispensed into the equipment) [CEB, 1992].

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

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

The photoresist is applied by a dispensing apparatus while the wafer is spinning at high speed in an exhausted enclosure. The excess photoresist from the application process is collected from the enclosure and disposed of, typically by incineration[3] [SIA, 2003]. The Semiconductor Onium Photoacid Generator (PAG) Consortium estimates that an average of 5.5 percent of dispensed photoresist containing onium PAG compounds adheres to the surface of the wafer [Semiconductor Onium PAG Consortium, 2017]. Additional industry information indicated that an estimated one to seven percent of the dispensed photoresist containing the chemical of interest may remain on the wafer [SIA, 2003] [ISESH, 2002], and the remaining "spun-off" material is disposed of. As a conservative estimate for water releases, EPA recommends assuming that up to seven percent of the dispensed photoresist remains on the wafer (wastes from developing, etching, and stripping are more likely released to water). Alternatively, incineration releases may be maximized by assuming one percent of the dispensed photoresist remains on the wafer.

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

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

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

Where:

$Elocal_{excess\_disp}$	=	Daily release of chemical of interest from application excess (kg chemical released/site-day)
Q_{chem_day}	=	Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4 of the 2010 ESD)
F_{equip_disp}	=	Mass fraction of chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into the equipment) (see Section 4.3 of the 2010 ESD)
F_{photo_wafer}	=	Mass fraction of the photoresist chemical applied that adheres to the wafer surface (default = 0.07 kg chemical adhered/kg chemical applied onto the spinning wafer) [SIA, 2003] [ISESH, 2002]

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

Developer solutions are a potential source of release of the chemical of interest [ISESH, 2002]. The developer solution is designed to remove either the exposed (positive) or unexposed (negative) photoresist from the wafer. The waste developer solution containing the removed photoresist is expected to be released to on-site industrial wastewater treatment [SIA, 2003] [Semiconductor Onium PAG Consortium, 2017]. EPA estimates that 50 percent of the

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

photoresist that adhered to the wafer surface, which was subsequently baked and exposed to light or other energy source, is removed in the development process[4] [CSM, 2002].

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

$$Elocal_{developer} = Q_{chem\_day} \times (1 - F_{equip\_disp}) \times F_{photo\_wafer} \times F_{photo\_develop} \quad \text{(Eqn. 4-4)}$$

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

Where:

$Elocal_{developer}$	=	Daily release of chemical of interest from developing (kg chemical released/site-day)
Q_{chem_day}	=	Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4 of the 2010 ESD)
F_{equip_disp}	=	Mass fraction of chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into the equipment) (see Section 4.4)
F_{photo_wafer}	=	Mass fraction of the photoresist chemical applied that adheres to the wafer surface (kg chemical adhered/kg chemical applied onto the spinning wafer) (see Section 4.5)
$F_{photo\_develop}$	=	Mass fraction of photoresist chemical removed in development (default = 0.5 kg chemical released/kg chemical adhered to wafer surface) [CSM, 2002]

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

Etching the wafer and applying the stripping solution removes the remainder of the photoresist from the wafer after the developing process. Etching is used to selectively remove metal from the surface of the wafer. The adhered photoresist masks portions of the wafer, protecting the masked surfaces from being removed during the etching process. Etching can be a wet process or a dry process [Nayak et al., 2011]. Wet etching involves submerging the wafer in a bath of liquid etching solution, in which the etching solution reacts with and removes the metal being etched. Dry etching utilizes plasma or etchant gas. In dry etching, plasma knocks off atoms from the wafer surface, whereas etchant gases react with the wafer surface, forming a bond with the atoms at the surface of the wafer and thereby removing those atoms from the wafer when the produced compound diffuses from the wafer. Because the function of photoresist is to protect surfaces of the wafer from etching processes, the majority of releases from this operation are expected to be from the subsequent stripping processes [Semiconductor Onium PAG Consortium, 2017].

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

Following etching, the remaining photoresist that is adhered to the wafer is removed via stripping. Industry information indicates that stripping can be done via plasma stripping/ashing, aqueous wet stripping, or organic solvent stripping [Semiconductor Onium PAG Consortium, 2017]. Plasma stripping is similar to plasma etching, in which ions in plasma bombard and knock off the photoresist atoms from the wafer. The knocked off photoresist then react with radicals in the plasma, thereby destroying the removed photoresist [Samco, 2018]. In aqueous stripping, an aqueous mixture containing some sort of acid and oxidizer is used to remove photoresist. The removed photoresist in the aqueous solution is typically treated as industrial wastewater before being discharged to a surface water or POTW [Semiconductor Onium PAG Consortium, 2017]. Solvent stripping utilizes an organic solvent to dissolve and remove photoresist. Organic solvent waste is typically incinerated or used for fuel blending. A portion of the solvent containing the removed photoresist may be rinsed off the wafer and treated as industrial wastewater at the semiconductor manufacturing site being discharged to a surface water or POTW [Semiconductor Onium PAG Consortium, 2017]. The Semiconductor Onium PAG Consortium estimates that 75 percent of waste from organic solvent stripping is incinerated and the remaining 25 percent is released to water, after being treated as industrial wastewater.

EPE recommends the following default media of release based on the type of stripping processes implemented:

- Plasma stripping/ash – chemical of interest in the removed photoresist is destroyed.
- Aqueous stripping – chemical of interest is released 100 percent to water.
- Organic solvent stripping – chemical of interest is released 25 percent to water and 75 percent to incineration.
- Unknown stripping process – chemical of interest is released to water or incineration.

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

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

(Eqn. 4-5)

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

Where:

$Elocal_{etch\_strip\_disposal}$	=	Daily release of chemical of interest (kg chemical released/site-day)
Q_{chem_day}	=	Daily use rate of chemical of interest (kg chemical dispensed/site-day) (see Section 3.4 of the 2010 ESD)
F_{equip_disp}	=	Mass fraction of chemical released as residual in process equipment (kg chemical released/kg chemical dispensed into the equipment) (see Section 4.4)
F_{photo_wafer}	=	Mass fraction of the photoresist chemical applied that adheres to the wafer surface (kg chemical adhered/kg chemical applied onto the spinning wafer) (see Section 4.5)
$F_{photo\_develop}$	=	Mass fraction of photoresist chemical removed in development (kg chemical released/kg chemical adhered to wafer surface) (see Section 4.6)

6.0 SAMPLE CALCULATIONS

This section presents an example of how the equations described in Section 4.0 of this document can be used to estimate releases of nonvolatile chemical additives found in a liquid photoresist used to manufacture semiconductors. Note that this section is numbered as Section 6.0, which is out of sequence from this document, to match the 2010 ESD on Photoresist Use in Semiconductor Manufacturing. The default values used in these calculations are presented in Section 4.0 and should be used only in the absence of site-specific information. The following data are used in this example calculation:

1. Chemical of interest production volume (Q_{chem_yr}) is *5,000 kg chemical/yr*.
2. Chemical of interest is 15 percent by weight in the photoresist formulation (F_{chem}) (nondefault; assumed to be known in this example).
3. The Following general facility estimates calculated in the 2010 ESD on Photoresist Use in Semiconductor Manufacturing are used for these sample calculations:
   - Q_{photo_day} = 36 kg photoresist dispensed/site-day
   - $TIME_{apply\_days}$ = 360 days/year
   - N_{sites} = 2.6 sites
   - Q_{chem_day} = 4.6 kg chemical dispensed/site-day
   - $N_{cont\_site\_yr}$ = 2,924 containers/site-yr

6.1 Release Assessments

6.1.1 Container Residues Released to Incineration (Release 1)

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

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

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

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

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

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

$Elocal_{container\_residue\_disp}$ = 0.0278 kg chem released/site-day

…over 360 days/year from 3 sites

Container residue should be assessed to incineration.

6.1.2 Equipment Cleaning Residues Released to Incineration or Landfill

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

$$Elocal_{equip\_disp} = 4.60\ \frac{kg\ chem\ dispensed}{site - day} \times 0.01 \frac{kg\ residual\ chem\ from\ equip\ cleaning}{kg\ chem\ dispensed}$$

$Elocal_{equip\_disp}$ = 0.046 kg chem. released/site-day

…over 360 days/year from 3 sites

Equipment cleaning residue should be assessed to incineration or landfill.

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

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

[Eqn. 4-3]

$$Elocal_{excess\_disp} = \frac{4.60\ kg\ chem\ dispensed}{site - day} \times \frac{(1 - 0.01) kg\ equip\ residue}{kg\ chem\ dispensed} \times \frac{(1 - [0.01\ to\ 0.07])\ kg\ chem\ adhered}{kg\ chem\ applied}$$

$Elocal_{excess\_disp}$ = 4.24 to 4.51 kg excess chem. released/site-day

…over 360 days/year from 3 sites

Spin-off release should be assessed to incineration.

6.1.4 Residual Photoresist Contained in Waste Developer Solution Released to On-Site Wastewater Treatment (Release 4)

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

[Eqn. 4-4]

$$Elocal_{developer} = \frac{4.60\ kg\ chem\ dispensed}{site - day} \times \frac{(1 - 0.01)\ kg\ equip\ residue}{kg\ chem\ dispensed} \times \frac{0.01\ to\ 0.07\ kg\ chem\ adhered}{kg\ chem\ applied} \times \frac{0.5\ kg\ chem\ released}{kg\ chem\ adhered}$$

$Elocal_{developer}$ = 0.023 to 0.16 kg chem. released/site-day

…over 360 days/year from 3 sites

Developer solution release should be assessed to on-site wastewater treatment.

6.1.5 Residual Photoresist Contained in Spent Etching and Stripper Solutions Released to On-Site Wastewater Treatment or Incineration (Release 5)

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

[Eqn. 4-5]

$$Elocal_{etch\_strip\_disposal} = \frac{4.60\ kg\ chem\ dispensed}{site - day} \times \frac{(1 - 0.01) kg\ equip\ residue}{kg\ chem\ dispensed} \times \frac{0.01\ to\ 0.07\ kg\ chem\ adhered}{kg\ chem\ applied} \times \frac{(1 - 0.5)\ kg\ chem\ released}{kg\ chem\ adhered}$$

$Elocal_{etch\_strip\_disposal}$ = 0.023 to 0.16 kg chem. released/site-day

…over 360 days/year from 3 sites

Because the type of stripping process is unknown, assume release is to on-site industrial wastewater treatment or incineration.

7.0 SAMPLE INITIAL REVIEW ENGINEERING REPORT (IRER)

See next page.

INITIAL REVIEW ENGINEERING REPORT CBI: No
Example Photoresist Use IRER

Contractor Draft 2/15/2018
ENGINEER: ERG
PV (kg/yr): 5,000 Import Only

SUBMITTER: Photoresist Application Company

USE: PMN is a component of a photoresist formulation (PMN is 15% of the composition) used for semiconductor manufacturing.

OTHER USES:

MSDS: No Label: No

TLV/PEL:

CRSS :

Chemical Name: Non-Volatile Photoresist Additive
S-H20: 1E-06 g/L @
VP: 1.0E-6 torr @ 20.00
MW: 200.00 %<500 %<1000
Physical State and Misc CRSS Info:

Consumer Use:

SAT (concerns) :
Migration to groundwater: Negligible to slow

PBT rating: P2B1T
Health:
Eco: Water (All releases to water with a CC =)

OCCUPATIONAL EXPOSURE RATING: NR

NOTES & KEY ASSUMPTIONS:
Generated by the 09/30/2013 version of ChemSTEER. All releases and exposures were assessed per the revised environmental release estimates for the 2010 ESD on Photoresist Use in Semiconductor Manufacturing. This IRER presents environmental releases only. Occupational exposures are outside of the scope of the ESD update and are not assessed in this sample IRER.

POLLUTION PREVENTION CONSIDERATIONS:

EXPOSURE-BASED REVIEW: No

INITIAL REVIEW ENGINEERING REPORT CBI: No

Example Photoresist Use IRER:

Use: Photoresist in Semiconductor Manufacturing

Number of Sites/ Location: 3

unknown site(s)

Days/yr: 360

Basis: Per the Revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing assume: Napply = 1,000 applications/site-hr, TIMEapply_hours = 24 hrs/day, Qapply = 1.5 mL photoresist/application, and TIMEapply_days = 360 days/yr. From these parameters, the daily use rate of photoresist is Qphoto_day = Napply x TIMEapply_hours x Qapply/1000 mL x density (assumed to be 1 kg/L) = 1,000 applications/site-hr x 24 hrs/day x (1.5 mL photoresist/application / 1000 mL) x 1 kg/L = 36 kg photoresist/site-day. With the daily use rate of photoresist, the daily PMN use rate can be calculated as (PMN is 15% in formulation per submission) = 36 kg photoresist/site-day x 0.15 kg chemical/kg photoresist = 5.4 kg chemical/site-day. CS calculates 2.6 sites. Rounding up to 3 sites, CS calculates a revised PMN use rate of 4.6 kg PMN/site-day.

Process Description: NCS is unloaded from 1-gallon (3.8-liter) bottles (liquid, 15%) --> charged to application equipment --> Application (spin-coat) --> Soft Bake --> Image application via radiation --> Hard Bake --> Developing --> Intermediate processing (e.g., baking) --> Etching --> Stripping --> PMN fully released or destroyed (Per Revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing)

ENVIRONMENTAL RELEASES ESTIMATE SUMMARY

IRER Note: The daily releases listed for any source below may coincide with daily releases from the other sources to the same medium.

Water
Output 2: 1.6E-1 kg/site-day over 360 days/yr from 3 sites
or 5.8E+1 kg/site-yr from 3 sites or 1.7E+2 kg/yr-all sites
to: On-Site Wastewater Treatment (per revised ESD)
from: Waste Developer Solution
basis: User-Defined Loss Rate Model. Per the revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing, RAD assumes that 50% of the adhered photoresist (Fphoto_wafer = 7%) is released during developing processes (Fphoto_develop = 50%). Per ESD, the loss fraction for this release is thus LF =(1-Fequip_disp) x Fphoto_wafer x Fphoto_develop = (1-0.01) x 0.07 x 0.5 = 0.03465. Per ESD, this release is to On-Site Wastewater Treatment.

Water or Incineration
Output 2: 1.6E-1 kg/site-day over 360 days/yr from 3 sites
or 5.8E+1 kg/site-yr from 3 sites or 1.7E+2 kg/yr-all sites
to: On-Site Wastewater Treatment or Incineration(per revised ESD)
from: Etching and Stripping Waste
basis: User-Defined Loss Rate Model. Per the revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing, RAD assumes that the remaining 50% of the adhered photoresist (Fphoto_wafer = 7%) is released during etching and stripping (1 - Fphoto_develop = 50%). Per ESD, the loss fraction for this release is thus LF = (1 - Fequip_disp) x Fphoto_wafer x (1 - Fphoto_develop) = (1-0.01) x 0.07 x (1-0.5) = 0.03465. Per ESD, RAD assumes this release is to On-Site Wastewater Treatment, as conservative, due to unknown type of stripping.

Incineration
High End: 2.8E-2 kg/site-day over 360 days/yr from 3 sites
or 1.0E+1 kg/site-yr from 3 sites or 3.0E+1 kg/yr-all sites
to: Incineration (per revised ESD)
from: Cleaning Liquid Residuals from Bottles Used to Transport the Raw Material
basis: EPA/OPPT Small Container Residual Model, CEB standard 0.6% residual. Per the revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing, RAD assesses this release with the EPA/OPPT Small Container Residual Model to incineration.

Incineration or Landfill
Conservative: 4.6E-2 kg/site-day over 360 days/yr from 3 sites
or 1.7E+1 kg/site-yr from 3 sites or 5E+1 kg/yr-all sites
to: Incineration or Landfill (per revised ESD)
from: Equipment Cleaning Losses of Liquids from a Single, Large Vessel

basis: EPA/OPPT Single Vessel Residual Model, CEB standard 1% residual. Per the revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing, RAD assesses this release with the EPA/OPPT Single Process Vessel Residual Model to incineration or landfill.

Incineration
Output 2: 4.3E+0 kg/site-day over 360 days/yr from 3 sites
or 1.5E+3 kg/site-yr from 3 sites or 4.6E+3 kg/yr-all sites
to: Incinerating (per revised ESD)
from: Spin-Off
basis: User-Defined Loss Rate Model. Per the revised 2010 ESD on Photoresist Use in Semiconductor Manufacturing, RAD assumes that 7% of the dispensed photoresist is adhered to the wafer (Fphoto_wafer), to maximize water releases. Per ESD, the loss fraction for this release is thus LF = (1-Fequip_disp)x(1-Fphoto_wafer) =(1-0.01)x(1-0.07) = 0.9207. Per ESD, this release is to incineration.

RELEASE TOTAL
5.0E+3 kg/yr - all sites

OCCUPATIONAL EXPOSURES ESTIMATE SUMMARY
Tot. # of workers exposed via assessed routes: 0
Basis:

Inhalation:

Occupational exposures are outside of the scope of the ESD update and are not assessed in this sample IRER.

Dermal:

Occupational exposures are outside of the scope of the ESD update and are not assessed in this sample IRER.

8.0 References

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