Appendix III

Semiconductor Photolithography Mass Balance Narrative

The SIA/SEMI coalition has met and corresponded with EPA a number of times regarding the October 18, 2000, proposed TSCA rule on PFOS[1]. The SIA/SEMI coalition developed a mass balance illustrating the input, uses, and eventual fate of PFAS materials in the photolithography process (see Attachment I).

This document provides supporting information for the data presented in that mass balance. The data was developed by SIA and SEMI based on our collective knowledge, expertise, and experience with photolithography technology and application. The data in each case are based on process knowledge and represent what we believe to be reasonable, worst-case values with reference to the amount of PFAS that might be discharged to wastewater.

The cumulative effect of these values over-predicts the quantity of PFAS that might be released to the environment. Examples of conservative estimates that will be further described in the narrative include PFAS supplies, the amount of PFAS in resist distributed through the photolithography process, and the amount of resist that remains on a wafer. This conservatism helps account for the uncertainties inherent in any mass balance so that engineering calculations of the total amount of PFAS that might be released to the environment is much higher than would be expected in practice.

I. PFAS Inputs – Data Acquisition and Completeness

A fairly small universe of suppliers provides liquid chemicals that serve the electronics industry. This is particularly true for a specialized electronic chemical product called photoresist. Just six companies provide greater than 90% of the world's photoresist.[2] These same companies also provide many of the ancillary products that are used in conjunction with photoresist (e.g., chemical strippers, removers, developers).

These chemical suppliers worked with their trade organization, SEMI, to develop a formal survey to quantify the PFAS consumption in North America in 2000 (Attachment II). For the photolithography data collected, each supplier calculated the PFAS consumption from their actual North American sales figures and the concentration of PFAS in their products. In addition, each supplier distinguished several other features about their PFAS contribution, including:

---

[1] SIA/SEMI introduced the term PFAS to represent the set of compounds that encompass all of the homologues of perfluoroalkane sulfonates. The term PFOS is reserved strictly for the C8 homologues of the PFAS family.

[2] "Electronic Chemicals: Riding Out the Downturn," Chemical Week, June 27 (2001): 23-28

- the function (surfactant versus photoacid generator (PAG)),
- technology application (photoresist, TARC, BARC, developer, etchant, polyimide, low-K dielectrics, and plating baths),
- homologue (C1-C4, C5-C7, C8, and C9), and
- SNUR status (listed versus not listed).

SEMI aggregated the values reported by individual suppliers. This preserved each company's confidential business information and promoted participation by the member companies. Given that the SNUR focuses primarily on C8 (PFOS) these inputs over predict the photolithography PFOS mass contributed to North America in 2000 for two reasons:

- the mass of the total surfactant or PAG molecule was used rather than just the PFAS portion of each molecule, and
- all homologues were included in the total mass rather than just the C8 homologue.

A version of the mass balance flow diagram presented to EPA during a July 10, 2001, meeting indicated that a total of 175 kg of PFAS was present in TARC products sold in 2000 for use in North America and depicted that 100 percent of this 175 kg of PFAS enters the wastewater discharge stream. Subsequent to that meeting, SIA/SEMI have learned that the total PFAS present in TARC products sold in 2000 in North America was 48 kg not 175 kg. This discrepancy was caused by one TARC supplier inadvertently responding to the SEMI survey with a worldwide, as opposed to North America, production number. A minor adjustment in the BARC volume from the 10 kg presented at the July 10 meeting to 15 kg also is necessary due to the inadvertent inclusion by another SEMI survey respondent of PFAS totals for BARC in its TARC numbers. This revised information was provided to EPA in an August 15, 2001, submission.

Subsequent to the August 15 information submittal, the SIA/SEMI coalition has received additional information regarding waste management practices at semiconductor companies using TARC products. The additional information obtained from surveys conducted by SEMI indicates that approximately 35% of semiconductor companies dispose of TARC material spun off of the wafer directly to wastewater rather than solvent waste. This change to the mass balance does result in a small change (16 kg) to the amount of PFAS that enters the wastewater discharge stream. While this does not represent a major change in the mass balance results, we have made appropriate changes to the model, as described below. Facilities that reported discharge of TARC to waste water are evaluating the feasibility of redirecting this waste stream to solvent collection or segregated disposal.

The SEMI survey also gathered data concerning polyimide use. The survey results have confirmed that some PFAS-containing polyimide developer products are being sold for use in North America. Polyimide and polyimide developer are organic products used in the photolithography process. SIA and SEMI believe that these materials would ultimately be disposed to a solvent waste collection system. The supplier of these

products has decided not to participate in our data collection effort, but also is not seeking an exemption from the SNUR. Therefore, no further polyimide use data collection or surveys on polyimide waste management have been conducted by SIA or SEMI. Similarly polyimide and polyimide developer are not included in the photolithography mass balance. SIA and SEMI are not currently seeking an exemption for the continued use of any PFAS-containing polyimide or polyimide developer.

II. PFAS Partitioning Coefficients

A core group of companies has been working on behalf of all coalition member companies in connection with PFAS issues. This core group represents 60 percent of the U.S. semiconductor market share[3] and includes most of the larger semiconductor companies. The partitioning coefficient data presented in the mass balance were derived based primarily on the process knowledge of this core group of companies. No formal survey tools were used.

A. Photo - Cleans

- 1% resist to cleans

  Within a coat track tool a known quantity of photoresist is applied to a wafer spinning at a known rate to achieve a given resist film thickness on the surface of the wafer. Excess resist is spun off of the wafer and collected via a coater bowl that is drained to a solvent collection system. As the solvents from resist evaporate the resist on the bowl surface may become hard and brittle presenting a source of contamination.

  Teflon bowls are used to decrease the surface tension between the bowl and the resist in order to maximize resist run off to the solvent collection system. Some residual resist may still occur on the surface of the coater bowl. Teflon bowls are removed from service to be cleaned approximately every two weeks depending on wafer throughput and resist application rate. Based on process knowledge and history with coater bowl servicing, we believe that 1% is a conservative estimate of the amount of residual resist that may remain on a coater bowl.

- 50% distribution between solvent and solid waste from cleans

[3] U.S.-based companies represented 50% of total, worldwide semiconductor market share in 2000. Companies participating in the PFAS effort represented 32% of total, worldwide market share. *Final 2000 Worldwide Semiconductor Market Share*, May 8, 2001, Gartner, Inc. Individual company market share is assumed to be similar within any of the regional markets (Americas, Europe, Japan, Asia Pacific). Regional semiconductor market share is roughly equivalent: Americas = 31%, Europe = 21%, Japan = 23%, Asia Pacific = 25%. *Taipei Forecast*, May, 2001, World Semiconductor Trade Statistics.

While a coater bowl is in service, periodic cleaning of the bowl may include the use of cleanroom wipes (employees conducting such operations would be wearing appropriate personal protective equipment to minimize exposure). Once contaminated with resist, these wipes would not be considered hazardous waste. However, the resist permanently stains the wipe making it ineligible for use within the cleanroom. Some companies may directly dispose of these wipes to common trash. Other companies may continue to utilize the wipes in non-cleanroom environments until the wipe has reached the end of its useful life. Even in that recycling atmosphere the wipe will eventually be placed in common trash. These types of manual cleans within the cleanroom environment are considered an exception rather than the rule due to potential product contamination that may occur.

Coater bowls must still undergo a more thorough solvent cleaning periodically. The solvent clean will remove stains and resist residue. Periodic solvent cleaning also insures that the coater bowl does not contribute to product contamination. The vast majority of resist removed from coater bowls occurs during the solvent cleaning operation.

Based on process knowledge and history with coater bowl cleaning SIA believes that a 50% distribution of PFAS between solvent and solid waste from cleaning operations is conservative. Solid waste contributions will be much smaller than 50% due to the infrequent nature of this type of cleaning. 50% to solid waste was chosen as a worst-case, conservative figure because common trash disposal of PFAS would result in a larger uncontrolled PFAS release (even though this is not expected to be the case).

- Chemical container handling

The photolithography mass balance does not explicitly address chemical containers. EPA had inquired about the handling and environmental management of used chemical containers.

Photoresist is packaged in either a one gallon glass or plastic NOW Pack® and a 2.5 gallon NOW Pack® bottle. A NOW Pack® is a hard plastic bottle that has an inner plastic bladder that is expanded during the filling process at the photoresist manufacture's plant before being filled with photoresist. All three types of containers are sealed at the photoresist manufactures facility. Containers are transported to semiconductor manufacturing facilities and then sent to the production line.

When the containers are connected to the dispensing or coating tool, "quick connectors" are used to draw the photoresist from the container into the coating bowl. Common industry practice indicates that one 200 mm wafer uses 2ml of photoresist. Since one gallon of photoresist costs approximately $2000.00 per gallon, the dispensing tools are designed to extract as much photoresist from the containers as feasible.

Any small amount of residual material that may be present in resist containers (usually less than a few milliliters) is typically drained into the solvent waste collection system. A residual film of resist may remain on the interior of containers due to surface tension. Any resist in these containers would be dry before disposal so PFAS containing liquids would not leak from the containers. Conservative estimates elsewhere in the mass balance (for example, the additional 1% (10.46 kg) of PFAS in resist [7% resist on wafer + 93% resist to solvent + 1% resist to cleaning = 101% PFAS from resist distributed through the mass balance]) easily over account for the miniscule quantities of PFAS that may be present in disposed resist containers.

Glass containers are either recycled or disposed to municipal solid waste. The inner bladder of NOW Pack® bottles is removed from the plastic container, dried, and is either recycled, disposed to municipal solid waste, or disposed as hazardous waste depending on local or state regulations. The outer plastic container, which does not contact the chemical contents, is either recycled or disposed to municipal solid waste. In all cases, glass and NOW Pack® containers are managed and disposed according to the requirements of 40 CFR 261.7, Residues of hazardous waste in empty containers.

B. Photo - Solvent Waste

- 7% photoresist/TARC/BARC on wafer / 93% resist/BARC to solvent waste / 60% TARC to wastewater

More empirical data is available for these coefficients than for the others. This is appropriate given that the majority of PFAS in the model is input at this point for the PAG and surfactant in photoresists. The percent of resist left on the surface of a wafer is determined by the properties outlined in Table 1.

Table 1. Variables for determining photoresist mass.

Variable	Range	Midpoint	Value Used	Rationale[a]
Liquid resist dispense volume	1.0 - 3.0 ml	2.0	2.0 ml	midpoint reflective of industry practice for 200 mm wafers
Thickness of resist film	0.3 – 2.0 μm	0.5 μm	0.5 μm	majority of circuit layers demand thinner resist [b]

Table 1. Variables for determining photoresist mass (con't).

Variable	Range	Midpoint	Value Used	Rationale[a]
Wafer diameter	100 - 200 mm	150 mm	200 mm	worst case for maximum resist carryover to develop step and wastewater discharge
Density of resist			$1.0\ g/cm^3$	
Resist solid content	10-20%	15%	15%	midpoint reflective of photoresists commonly used with 200 mm wafers

a. Values used reflect the reasonable, worst-case prediction of the amount of PFAS that might be discharged to wastewater.

b. Higher resolution, which is critical for small circuit features, can be obtained with thinner resists. In some cases a thicker resist film is required for resistance to subsequent process steps (e.g., high-energy implant or deep contact etches). A resist that is too thin would break down during these processes. Less than 15% of the steps require a thicker resist film.

(1) Weight of resist film per wafer after baking dries solvent
[wafer area] x [film thickness] x [resist density]

$$\left[3.1416\,x\,\frac{(200mm)^2}{4}\right]x\left[0.5\,um\,x\,\frac{1mm}{1000um}\right]x\left[\frac{1.0g}{cm^3}\right]x\left[\frac{1cm^3}{1000mm^3}\right]=0.0157g$$

(2) Weight of total solids in dispensed resist
[resist dispense volume] x [resist density] x [resist solid content]

$$2.0ml\,x\,1.0g/ml\,x\,0.15=0.3g$$

(3) Percent of total resist solid left on wafer (resist film)
[weight dried resist film] / [weight of total solids in resist]

$$0.0157g/0.3g\,x\,100=5.2\%$$

SIA believes the values presented in Table 1 represent reasonable worst-case estimates. An additional level of conservatism is used by assuming that 7%, instead

of 5%, of the resist remains on the wafer for subsequent processing in the develop step. 93% of the resist would go to solvent waste collection. The same variables are used for allocating the percentages of BARC that stays on the wafer (7%) and that would typically go to solvent waste collection (93%). The 7% assumption is even more conservative for TARC and BARC use because those products are applied as even thinner films. We expect the amount of TARC or BARC left on a wafer after the photo step could be as low as 1% of the volume dispensed onto the wafer.

Waste management practices for TARC are currently different than for BARC. The 93% of TARC input that does not remain on the wafer can be disposed two different ways. Based on currently available data derived from a supplier survey of TARC applications, it appears that approximately 65% of TARC waste or 60% of PFAS input (i.e., 65% of 93%) would be discharged to solvent waste. The remaining 35% of TARC waste or 33% of PFAS input (i.e., 35% of 93%) would be discharged to waste water. Therefore, a total of 40% of TARC PFAS input is shown in the mass balance between the Photo and Develop steps (7% TARC input on wafer + 33% TARC input to wastewater).

These calculations were derived on a per wafer basis. Rather than attempting to quantify the amount of wafers processed by semiconductor manufacturers we simply applied these percentages to the total mass of PFAS the suppliers provided to semiconductor manufacturers (see Section I).

C. Develop

- 100% developer to waste water

Resist is applied to the wafer and dried by baking. The wafer is then exposed to light. The light alters the exposed areas of the resist film and induces a change in solubility characteristics. The more soluble areas can be developed or washed away and would be discharged to waste water by the semiconductor facility to a publicly owned treatment works. Developer carried over on the wafer to any subsequent manufacturing steps would be considered a contaminant. A thorough rinse with deionized water insures that no developer contamination will occur. Therefore, 100% of the PFAS in developer will be sent to waste water.

Subsequent to the July 10, 2001, meeting with EPA, SIA and SEMI have obtained additional information indicating that non-PFAS alternatives now have been identified for the PFAS-containing developer products. Hundreds of hours already have been invested to identify non-PFAS alternatives and to develop the conversion strategies necessary to ensure equivalent technical performance and to minimize down time and loss. Hundreds more hours will be required to qualify and fully convert to these alternatives. Such a resource-intensive process is necessary before substitution can occur because experience has shown that changing the surfactant in developer products can cause a range of defects -- including potentially even complete device failure. To address the problem of defects, therefore, electronic

device manufacturers must undergo a rigorous qualification process before implementing new developer products. As a result of this transition, the PFAS contribution from developer products to the wastewater discharge stream will reduce to zero at some point in the future.

- 50% resist film to wastewater / 50% resist film on wafer

Soluble areas of resist film exposed to light are developed off the wafer. Areas of resist film not exposed to light would stay on the wafer through the develop step and on to other semiconductor processes (diffusion, implant, etc.).

The open area on the wafer (see Table 2) determines the amount of resist film remaining on the wafer after exposure. The open area on the wafer is the amount exposed to light (the percentage of resist that would go to wastewater).

Table 2. Variables for determining PFAS mass to waste water

Variable	Range	Midpoint	Value Used	Rationale
Open area on wafer	1 - 98%	20 - 40% avg.	50%	industry average

- 50% wafers processed by Dry Strip / 50% wafers processed by Wet Strip

The resist film is used to protect or expose specific portions of the wafer during subsequent process steps as the circuit layers are built. After the resist film has served its purpose in these other process steps the resist film must be removed or stripped from the wafer surface. The main objective of photoresist stripping is complete removal of the resist film without adversely affecting the wafer surface and without leaving any contamination residues on the wafer surface. Either dry stripping or wet stripping may be used depending upon the previous and subsequent process steps and depending upon the material underlying the resist film.

Photolithography comprises 150 of the 500 major steps in the complete manufacturing process for any given product type. A particular company may produce many different product types so there are many possible variations for when dry strip or wet strip may be required. Based on process knowledge the SIA believes a 50% distribution between dry and wet strip is reasonable.

D. Dry Strip

- 100% destruction of PFAS in Dry Strip

Dry stripping of resist film is accomplished by exposure to reactive plasma. Reactive plasmas are not a thermal degradation process. The term reactive plasma is meant to describe a discharge in which ionization and fragmentation of gases take

place and produce chemically active species, frequently oxidizers and/or reducing agents. Such plasmas are reactive both in the gas phase and with solid surfaces exposed to them.[4]

In production, wafers are loaded into the reaction chamber and a vacuum is pulled. The oxygen is then bled into the chamber at a rate of several hundred cubic centimeters per minute, followed by rf energy, which is inductively coupled to the gas at a fixed frequency. The rf energy excites the oxygen, creating the active species (most of which is atomic oxygen) that reduce the resists' polymeric chains to simpler and lower-molecular-weight groups.[5] Other gas components besides oxygen may be used for other purposes such as reducing inorganic contamination.

This plasma reaction at the molecular level reduces any organic matter including PFAS. This is not an ion bombardment process where energetic ions would physically displace 'chunks' of resist containing PFAS that may be released from the tool. This is the only way that PFAS could survive intact and be released from the dry strip reaction chamber. The plasma generation is actually located a remote distance from the reaction chamber to prevent precisely that type of ion bombardment which could significantly damage the wafer surface.

The end purpose of any plasma resist strip is to completely remove all of the resist film from the surface of the wafer. Any resist film that remains on the surface would be a contaminant to subsequent process steps. Based on the aggressive plasma conditions in the dry strip tool, the contamination control requirements, and based on process knowledge the SIA believes 100% destruction of PFAS occurs during dry strip.

E. Wet Strip

- Identity of wet strip chemicals

There are a variety of chemistries that may be used for the wet strip process. Three of the most common include N-methyl-2-pyrrolidone (NMP), propylene glycol monomethyl ether acetate (PGMEA), and sulfuric acid. Based on SIA process knowledge the other chemistries comprise a smaller fraction and would not materially change the PFAS fate from this part of the mass balance. Some of the wet strip chemistries may be discharged to wastewater but the most common disposal method of the three primary wet strip chemicals is recycling (see Section III below). Again, the fraction that may go to wastewater will not materially change the PFAS fate from this part of the mass balance (a 10% change would amount to an additional 2 kg going to wastewater).

[4] S. M. Sze, VLSI Technology, 1988.

[5] David J. Elliott, Integrated Circuit Fabrication Technology, 1982.

- 33% distribution between three chemistries

  This distribution is an estimation based on SIA process knowledge. Any different distribution would not affect the PFAS fate from wet strip. The chemicals are recycled into other commercial products. Changing to a 20/30/50 distribution, for example, would not change the ultimate fate of the 18kg of PFAS in recycled industrial materials.

  The ultimate fate of the recycled industrial materials or their PFOS components cannot be quantified since these materials are frequently not used in the semiconductor industry. We were therefore not comfortable designating these materials as being incinerated or sent to waste water. Based on the material properties of, however, it is reasonable to assume that two of the three materials (NMP & PGMEA) would eventually be treated by incineration.

III. PFAS Outputs - Waste Management Practices Survey

The application and fate of PFAS in photolithography is relatively straightforward. However, given the complexity and variability of semiconductor products a survey was distributed to SIA member companies. The purpose of the survey was to confirm that the SIA/SEMI group had captured all of the relevant disposal pathways for PFAS input at the photolithography step. The survey tool used can be found in Attachment III. Companies were directed to identify any other potential non-wastewater waste streams and any other disposal management practices for photolithography related waste materials.

All of the responses received confirmed the PFAS fate as outlined in the mass balance. Additional waste streams were not identified by anyone nor were there any additional disposal methods. Based on our process knowledge and this survey, we believe the mass balance captures the entire potential fate of PFAS used during photolithography.

IV. Relevance of Model to Other Uses in Electronics Industry

The mass balance model presented to EPA has been focused to date on semiconductor manufacturing. There are other photolithography applications in the electronics industry that are virtually identical to those in semiconductor manufacturing. Two non-semiconductor examples are provided below. They involve magnetoresistive head wafer manufacturing and thin film manufacturing. The use of PFAS photoresists in these other uses has already been accounted for by the SEMI supplier survey data and, therefore, by the mass balance. Based on input we received from material suppliers, non-semiconductor manufacturing processes accounted for 5 percent or less of PFAS photoresists sold in 2000.

In the manufacture of magnetoresistive head wafers, a series of photolithography steps is used to create a pattern on a wafer, which is ultimately cut into individual read-write heads that are installed into hard disk drives. The primary differences between the

magnetoresistive head wafer manufacturing process and the semiconductor manufacturing process are: 1) the resist film used in magnetoresistive head wafer manufacturing tend to be thicker and, 2) the size of the wafers used in head manufacturing are smaller. The composition of the photoresists may also vary.

Another example involves multi-level thin film manufacturing of chip carriers. In the multi-level thin film manufacturing process, a series of photolithography steps is used to create a pattern for multiple levels on a ceramic substrate, which is ultimately installed into high-end servers. The primary differences between the multi layer thin film manufacturing process and the semiconductor manufacturing process are: 1) the resist film used in the multi-level thin films manufacturing tend to be thicker; 2) the feature size is much larger and, 3) the carriers are ceramic substrates on which the multi-level thin film manufacturing is processed. The composition of the photoresists may also vary.

7115250