Appendix I

Background Information on Electronics Industry, Photolithography and PFAS Use

The purpose of this appendix is to provide background information on certain technical and economic aspects of the electronics industry, the importance of photolithography in manufacture of advanced electronics and the role of PFAS materials in manufacturing processes.

I. Technological and Business Dynamics of the Electronics Industry

A. The Demand for Innovation in Electronics

Electronic devices are core technologies in our society. Besides their importance in computing and telecommunications, they are increasingly important in all aspects of manufacturing and service industries. As an example, microprocessor technologies have been essential to advances in medicine, powering innovations in genetic screening of drugs, analysis of body functions and tomography.

Advanced electronics also play a critical role in the advancement of public policy objectives. The U.S. armed forces increasingly look to high-end electronic technologies to provide our essential edge in addressing foreign threats, through smart weapons, intelligence gathering and analysis, and battlefield communications.[1] EPA's own environmental objectives are also served by advances in monitoring technologies, energy efficiency, environmental forecasting, and industrial process efficiency that depend on innovations in electronics.

For all of these purposes, the electronics industry faces a constant demand for new products and must maintain a capacity for innovation in order to keep pace with customer needs.

B. High Levels of Competition

The significant growth in the manufacture of electronic devices is explained in part by the rapid technological advances made by the industry. Manufacturing processes for electronic devices are in constant evolution as a competitive necessity. For instance, the density of transistors placed on the top end microprocessors has doubled approximately every 18 months from 275,000 in 1985 to approximately 8 million today – all of which are placed on a die that is roughly the size of a fingernail. As semiconductor manufacturers are able to continue to

[1] In some national defense applications, microprocessor technologies are supplied under special contracts that prevent reliance on foreign suppliers for key materials, necessitating a domestic capacity to manufacture such materials.

miniaturize circuit features, they are able to produce more die on a single wafer for roughly the same production cost thus increasing their competitiveness.

Due to ever greater competitive demand for innovation, however, new electronic products become obsolete more quickly than in the past. As a result, companies are forced to make changes in product lines in order to compete in the global marketplace, control costs, maintain quality, and meet corporate pollution prevention goals. Even a one-week delay in a new product announcement or its shipping date can result in substantial lost revenues, and more importantly, may adversely impact the product's ultimate success. Due to the global competitive dynamics of the electronics industry, only companies that swiftly implement change will retain existing markets and/or capture new markets.

C. Product Cycles of Short Duration

Many of the products sold by the electronics industry generally have short useful lives for our customers due to the constant demand for increased performance and smaller size. Examples of this can be seen throughout the consumer spectrum, including pocket-sized cell phones and organizers, both smaller and larger but thinner televisions, and faster and significantly cheaper computers. It is not enough to simply change the exterior styling and choice of interior options, as in the automobile industry for example. Were the automobile industry to have proceeded with development and corresponding unit cost reductions at the same pace, a car costing $18,000 in 1985 would cost less than $100 today.

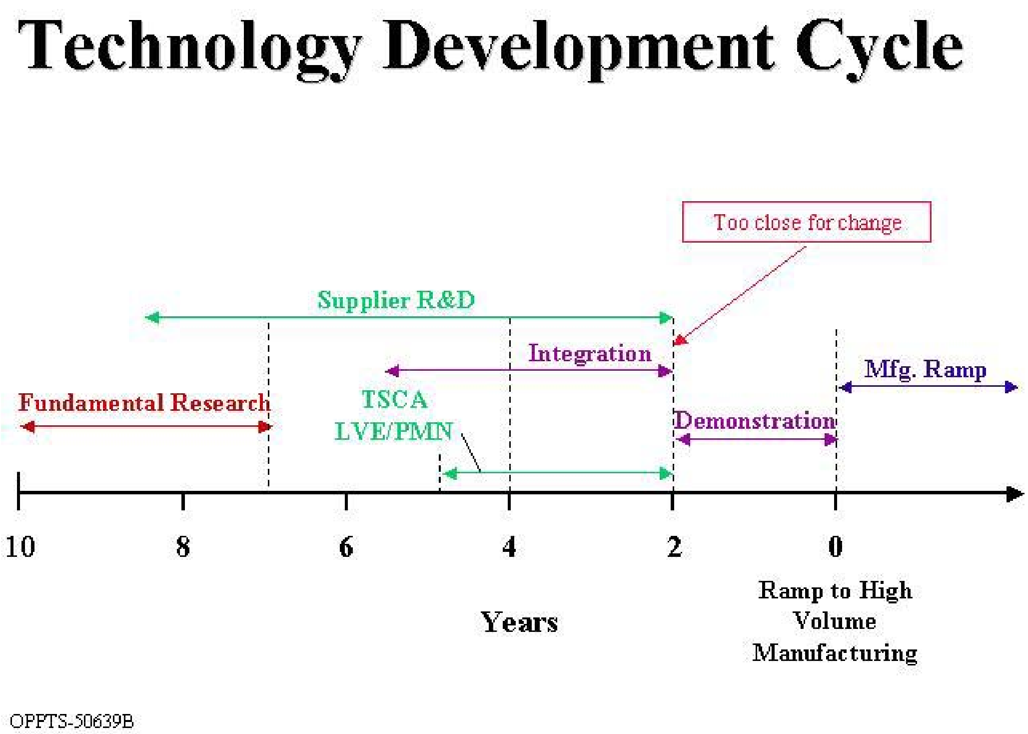
The technologically dynamic nature of the electronics industry distinguishes it from traditional manufacturing sectors. Demand for new, smaller and faster products drives the electronics industry to make process changes in-line during the manufacturing process. Indeed, to avoid obsolescence, a typical semiconductor manufacturing facility will undergo numerous chemical and equipment changes in the span of a single year. These changes can decrease the cycle time to produce a given product, increase the manufacturing yield or decrease the unit production cost.

These process "tweaks" can include alterations such as flowrate, temperature or adjustments to process chemistries. They can also include the installation of new equipment that has a process advantage over the older equipment. Semiconductor capital equipment purchases typically have a useful life of only three to five years. These frequent process tweaks and equipment upgrades are necessary to make minor changes to existing product lines or for entirely new product lines utilizing existing technology. The precise number of process steps, their sequence or the chemicals and equipment used for a single product are often very different between the time a product is first built and its final production run.

D. Long Technology Development Cycles

The fact that product cycles are relatively short does not necessarily imply that the electronics industry can make all forms of technology change easily and quickly. The processes for manufacturing electronic devices are quite complex and interdependent. As a result, some forms of technology development can take years to complete.

Within the electronics industry, there are significant development hurdles that must be overcome before many upgrades and innovations can move into production. Many of these developments involve basic research of the most fundamental kind. In these cases, changes may be years in the planning. Some technology changes in the photolithography area, including the development of new photo-acid generators (PAG's) in photoresists, will take time to develop. The following chart summarizes the major stages of the technology development cycle:



Within the broad stages outlined above, companies must engage in several steps to convert to new process chemistries. The process of qualifying new materials for production begins in the laboratory at the photoresist supplier. Researchers develop new formulations and test them at the applications facilities. After completing a rigorous screening process, a select few samples are introduced to the customer for testing. Every new chemical introduced for evaluation at a customer site passes through a chemical approval system. A team of experts reviews the Material Safety Data Sheet (MSDS) for each new chemical; this team identifies opportunities for pollution prevention, waste minimization, and recycling, and rejects chemicals if they do not meet the safety requirements of the manufacturing facility. After a new chemical is approved for customer evaluation, lithography engineers test and benchmark the technical performance of the new materials against the existing process and chemical. Feedback is provided to the supplier, and often there is an iterative course of reformulation and testing before a final material is selected for qualification.

Electronic device manufacturers must carry out scrupulous qualification procedures before switching to new materials. These procedures may vary from facility to facility, but the intent is to protect the existing product and manufacturing process from deviations, yield loss, and reliability issues that can result from minor changes to the process. Prior to conversion, many semiconductor manufacturers insist on qualifying multiple batches (at least three) of the new material to determine if the supplier can repeatedly manufacture the product to certain specifications. Taking developer as an example, these specifications include metals, particles, normality, and post-develop defects. Photoresists are tested to these and more specifications, including photospeed, viscosity, water content, and optical parameters. Often analytical tests are performed at both the supplier site and the customer site. Concurrently, the device manufacturer will commit to running multiple (5-10) split lots, where half of the wafers employ the experimental material and half of the wafers exercise the control material. After split lot yield is comparatively successful, as many as forty lots with the new material are processed and tested before final conversion is achieved.

To succeed in this competitive environment, suppliers must employ leading edge materials technology to meet constantly evolving, stringent performance requirements early in the technology development cycle. Given the emphasis on performance in the electronics industry, suppliers and device manufacturers must have access to materials that enable competitively advantaged products or else risk losing business to foreign competitors.

II. Chemical Stewardship in the Industry

A. Stewardship Activities

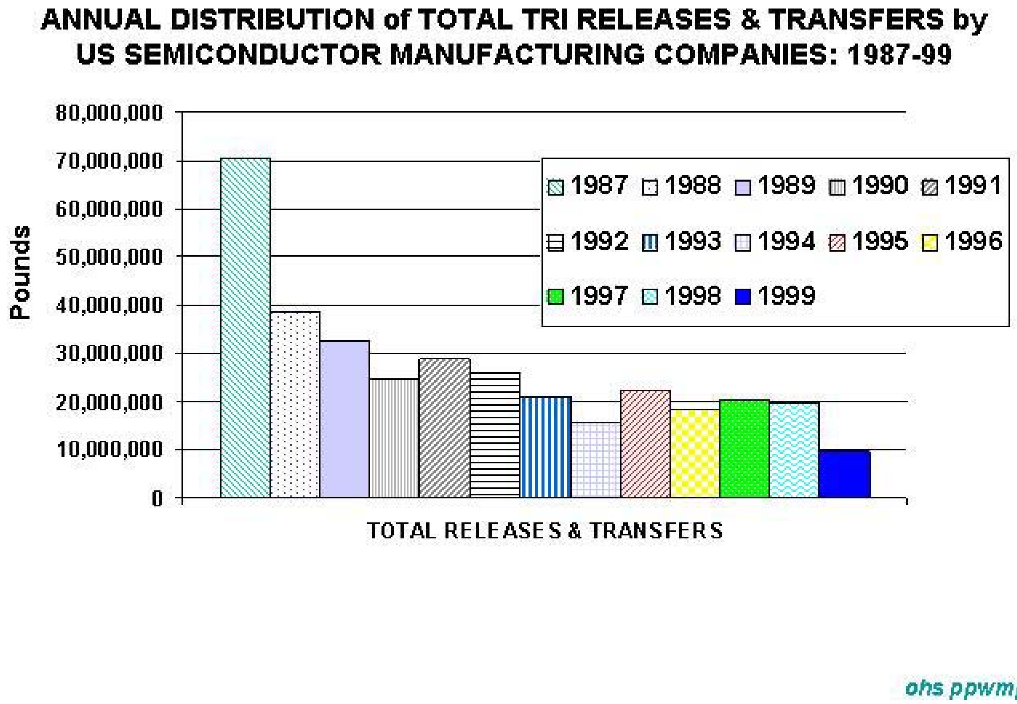
The US semiconductor industry has a tradition of providing a safe, healthful workplace and of handling manufacturing wastes, both hazardous and non-hazardous, in a manner that protects the environment. The industry's injury and illness record under OSHA typically places the semiconductor industry among the five industries with the lowest reportable incidents for durable goods manufacturers. In fact, the most recent Bureau of Labor Statistics tabulation (1999) placed the semiconductor industry at an injury and illness rate of 2.2/100 employees, the second lowest amid 208 durable goods manufacturers. Many of our members are participants in OSHA's Star and Merit programs.

The SIA has funded evaluations of the risk associated with the use of glycol ethers for photoresist formulations, and championed the adoption of safe solvents. In addition, we are currently funding an independent evaluation of potential cancer risk among cleanroom workers. We support this effort through a very active technical committee consisting of experienced, knowledgeable health and safety professionals from our member companies. Over the years, this committee has sponsored technical symposiums on health and safety aspects of semiconductor manufacturing, co-sponsored by organizations like NIOSH and OSHA.

We believe that our programs to protect the environment, like our health and safety programs, are second to none. Many of our members are ISO 14000-certified and some are participants in the USEPA Project XL initiative. Our environmental programs have a history of cooperation and sharing between our member companies. As for our health and safety committees, experts from our member companies support environmental committees. Some notable accomplishments of the industry through these committees have been the dramatic reductions achieved in TRI reportable emissions (see TRI release figure below), the conversion of all HAPS major sources to synthetic minors, the elimination of the use of ozone-depleting substances in semiconductor manufacturing, and participation in a voluntary agreement with the USEPA to voluntarily reduce PFC emissions from our manufacturing operations.

SIA is a founding member and participant in the World Semiconductor Council (WSC) and it's Environment Safety and Health (ESH) Task Force. The WSC, comprised of top executives from the leading semiconductor manufacturers from the United States, Japan, Europe, Korea, and Taiwan, was established to improve worldwide trade relations. Under the leadership of the WSC, the ESH Task Force was established with an initial mission to evaluate the issue of global climate change and what the global semiconductor industry could do to effect emission reductions. In response to this charge, the ESH Task Force was able to secure a global agreement between most of the major producers of semiconductors worldwide, to reduce PFC emissions to a level 10% below emissions from the baseline year. This global agreement, enacted in April 1999, represents the first example of a global industry initiative to voluntarily unite to work towards a common solution to a common problem. For these efforts, the WSC was awarded the EPA Climate Protection Award in 1998. Subsequently, several semiconductor companies have been awarded individual Climate Protection Awards.

In terms of our management of toxic chemicals, the following chart shows that we have made steady progress in reducing our releases of Toxic Release Inventory (TRI) chemicals:



B. Alignment of Environmental and Business Objectives

The commitment of the electronics industry to chemical stewardship has a strong basis in corporate ethics, but this commitment is also reinforced by key aspects of our business and technological profile.

1. Product Cycles

As mentioned above, the product lines of the electronics industry are in a constant state of change. These changes create opportunities for our companies to institute process changes and product characteristics that serve both technological and environmental stewardship purposes. Our companies frequently make use of these opportunities to advance multiple objectives. Many of the initiatives mentioned in the previous section could be implemented quickly because of the dynamic product cycles in the industry.

2. Efficiency in Materials Use

As mentioned earlier, the electronics industry is highly competitive, requiring companies to search continually for new ways to reduce costs. A key technological approach to cost reduction is to find way to be more efficient in the use of materials. This drive for efficiency in materials use aligns well with the pollution prevention ethic. The alignment of these objectives has yielded several success stories within our industry. In section III.B. below we describe a particular example of this trend related to the use of photoresists in photolithography.

3. Worker Protection and Quality Control

As SIA and SEMI have pointed out throughout this rulemaking, the electronics industry has had a strong record in providing worker protection in its facilities. Clearly this record is built upon the desire of our companies to provide for a healthy workplace and to comply with applicable safety requirements.

In addition, this philosophy is reinforced by the high levels of quality control that must be maintained in electronics manufacturing. The processes we use must be capable of great precision and a low tolerance for contamination of the circuitry in our products. A contaminated circuit represents a failed product. A key element of our quality control strategy is the separation of products from human contact during manufacturing. The tools and handling practices used on the majority of our production lines are designed to prevent direct worker contact with the product.[2] This strategy has clear benefits for the workers, preventing any substantial exposure to the chemicals used in the process.

Several SEMI and SIA member companies have conducted industrial hygiene air monitoring to confirm that there is no inhalation exposure to PFOS compounds during semiconductor manufacturing. This monitoring was conducted at multiple chip fabrication facilities and at two photoresist manufacturing facilities. Multiple personal and area air samples were collected during routine operations and during tasks which were believed to represent the greatest exposure potential. For example, a photoresist manufacturer monitored personnel engaged in transferring PFOS surfactants into their photoresist blending vessels and also monitored in an area within inches of the vessel's charging manway.

All personal and area samples collected at operations involving PFOS liquids (e.g., surfactants, photoresists and ARC's) utilized 3M's recommended method and laboratory. No detectable PFOS was reported for any sample (<0.007 milligrams/m3 detection limit). In addition, personal samples were collected at a photoresist manufacturing facility using NIOSH Method 0500 to monitor for particulates associated with transferring solid or crystalline PFOS substances (PAG's) to a photoresist blending vessel. No detectable particulates were observed in any sample (<0.02 mg/m3 total particulate detection limit).

[2] For example, to protect employees and due to the critical nature of the purity of the photochemicals used, the dispense area in the equipment is protected from the environment external to the equipment by a localized containment system. During the application of photochemicals, the localized containment system is vented under vacuum to an appropriate air pollution control device. Additionally, the air in the external environment is constantly filtered to maintain the air purity needed to manufacture semiconductors.

The lack of detectable PFOS in personal and area air samples correlates well with the physical and chemical properties (vapor pressure) of the PFOS substances. In addition, because of the standard use of appropriate personal protective equipment, SEMI and SIA companies feel that there is also good protection against any dermal exposure to PFOS compounds.

III. Importance of Photolithography and Use of PFOS

A. Significance of Photolithography

While many steps are involved in the manufacture of modern electronic components, it is well recognized that the photolithography process is absolutely critical in defining the level of sophistication and performance of our technology. A key element of advanced electronics is the ability to create powerful circuitry at increasingly smaller scales. This has been made possible through continual shrinking (or miniaturization) of the size of the individual circuit elements of a chip.

Miniaturization refers to the ability to separate two objects by smaller and smaller spaces, termed optical resolution. The ability to effect this separation is proportional to the wavelength of light that is used to pattern the separation. To improve resolution, the semiconductor industry has shortened the wavelength that it uses in photolithography three times since 1980, from 436nm to 365nm, then to 248nm and recently to 193nm. A fourth wavelength, 157nm is expected to be introduced in 2004-5. This shortening of wavelength, however, comes at a price; the composition of the photoresist must be adjusted to appropriately respond to whichever wavelength is used for the exposure.

The semiconductor industry continues to make many products with 436nm and 365nm photolithography for which further miniaturization is no longer cost effective. These products do not require PFOS PAG in the photoresist. The semiconductor industry is accelerating the incorporation of 248nm lithography. This is particularly evident from the purchases of photolithography equipment for this wavelength. This trend may slacken without access to the PFOS products critical to the performance of 248nm photoresists and ARC materials.

The semiconductor industry is just beginning to introduce 193nm photolithography. Photolithography at 193nm is expected to be the technology that drives the next round of miniaturization, the so-called 100nm technology node, in 2003-4. Without PFOS PAGs, this drive will stop. Some other photolithography would need to fill the gap, or the 100nm node will be delayed or missed. The International Technology Roadmap for Semiconductors lists some options, but industry confidence in them, as evidenced by equipment purchases, has not materialized. Photolithography with 157nm wavelength is one option, but all current knowledge suggests that 157nm photoresists will also require PFOS PAG's.

The other options are lumped together as non-optical, or next generation lithography. In general, the next generation lithography options are not mature and require significant infrastructure development. If they are required for the 100nm technology node, the node will be quite late, with a consequential slowing of benefits from the electronic revolution.

As lithographic methods incorporate shorter wavelength sources and more transparent resists, control of reflectivity to values near a few percent becomes more critical. Simply put, stray reflection causes loss of contrast. In more severe cases where light is reflected into regions that were not intended to receive exposure, reflective “notching” can cause device failure.

To reduce the reflectivity at the resist-substrate interface, an intermediate film called a bottom anti-reflective coating (BARC) can be coated beneath the resist. To reduce the reflectivity at the resist-air interface, a film called a top anti-reflective coating (TARC) can be coated on top of the resist. Both types of reflection control materials are critical to successful pattern definition in the photolithography process.

These reflection control materials incorporate PFAS into their design, either as surfactants for BARC or as PFAS-derivatives for TARC. These ARC materials rely on PFAS to provide an exact refractive index as well as needed film-forming characteristics to meet performance objectives.

B. Reduced Use of Photoresists

The volume of photoresist used per layer in chip manufacturing has been reduced over time from ~8.0 ml in the early 1990s to 2.0 ml today. Irrespective of the trend toward increasing wafer diameter, the industry is anticipating further reduction in photoresist volume per layer in the direction of 1.0 ml. Generally, the dispense volume is optimized to attain a desired layer thickness, uniformity, and defectivity. Most of the resist applied to the wafer during the coating step is spun off to ensure a uniform, yet very thin layer of resist on the wafer surface.

Photoresist volume reduction involves a method of applying a solvent pre-wet to wafers to reduce the amount of photoresist required to coat the wafer without compromising desired target thickness. The coating recipe is modified to add a solvent dispense step prior to the resist dispense step. This solvent pre-dispense step prepares the wafer surface to enable the resist to spread more easily over the wafer, thereby requiring less resist to coat the wafer. The modified recipes result in a reduced consumption rate for the resist, and a slightly increased usage of solvent for pre-dispense. The net effect, as summarized in Table 1, is a reduced chemical usage of approximately 4 ml per wafer; the amount of photoresist used can be reduced from 8 ml/wafer to 2 ml/wafer using this technique.

Table 1.

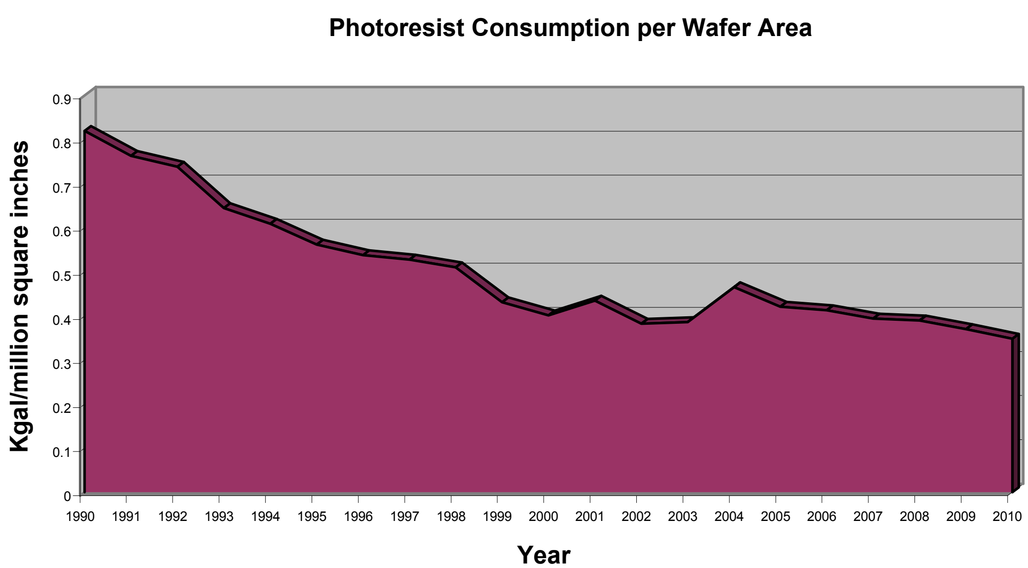
Solvent	Original Vol. (ml/wafer)	Reduced Vol. (ml/wafer)	Reduction (ml/wafer)
Pre-dispense (solvent)	0	2	-2
Photoresist	8	2	6
Total	8	4	4

The effect on the amount of excess resist spun off the wafer and collected in the solvent waste system is determined from the mass balance, given a resist thickness of 0.5μm, and shown in Table 2. When using a decreased resist volume per wafer, the amount of resist to solvent waste decreases. In the August 15 submission to the EPA, a worst-case estimate was that 7% resist solid remains on the wafer when resist volume is fixed at 2.0 ml. Table 2 demonstrates that further reductions in resist volume toward 1.0 ml will not dramatically change the percent of resist solid left on the wafer.

Table 2.

Resist Volume (ml)	% Resist to solvent waste	% Resist solid left on wafer
8	99	1
5	98	2
3	97	3
2	95	5
1	90	10

Another aspect of the optimization equation is the increase in wafer size from 150mm (1995) to 200mm (2000) to 300mm (2005) and simultaneous increase in die produced per square mm of silicon due to design shrinks. The result is a net decrease in photoresist used per device over time. The figure below shows the reduction in photoresist consumption per wafer area over time, projected to 2010.



Sources: Dataquest, Prismark, SEMI

Resist thickness reduction can also influence the amount of resist going to wastewater; thinner films increase the percentage of resist going to incineration. Resists are spun to different thickness to satisfy different requirements. The best resolution is often obtained with thin resists; however, resist films need to be thick enough to serve as etch masks or to block ion implantations. High-resolution lithography today typically employs resists with thickness in the range of 0.3-0.5µm, while in the past the typical thickness was between 1.0 and 1.5µm. Table 3 shows the affect of thinner films on the percent of resist solid left on the wafer, at a constant resist volume of 2.0 ml. Thus, thinner films increase the percentage of resist going to incineration when the resist volume is constant.

Table 3.

Resist Thickness (μm)	% Resist to solvent waste	% Resist solid left on wafer
0.7	93	7
0.5	95	5
0.4	96	4
0.3	97	3
0.2	98	2

Lithography engineers are in the business of process optimization. They are continuously engaged in projects that focus on reducing consumables, minimizing waste, testing new materials and processes, optimizing equipment, and increasing productivity. IC manufacturers often work in close cooperation with photoresist suppliers to evaluate new formulations and improve existing formulations.

The same variables can be correlated to both TARC and BARC. These ARC materials, however, have thinner films compared to photoresists, which means that the total quantity of ARC used is significantly lower than the volume of photoresist used in the same process.

C. Stewardship Activities Identify Replacement Opportunities

As indicated in the August 15, 2001 SIA/SEMI letter, non-PFAS alternatives for surfactants in developer products have now been identified and successfully qualified in at least one facility. More U.S. semiconductor manufacturers will begin the process to qualify and fully convert to alternative developers. Once PFAS in the developer is eliminated, the PFAS going to wastewater from the photolithography process will be significantly reduced.

While the specifics of this conversion process involve proprietary information, the following description provides EPA with some of the steps that are generally involved in requalification of developer materials. Developer requalification involves contrasting measured chemical and functional parameters of potential alternative products with PFAS-containing products. This determines whether substitute products are even viable alternatives to offer to device manufacturers. The challenge for device manufacturers in successfully replacing developers is that many device manufacturers use just one or two developers for dozens of different photoresists. Since each photoresist provides a unique performance characteristic for a given application and resulting device feature, the interactions between the developer and entire photolithographic process must be fully characterized through rigorous and time-consuming Failure Modes and Effects Analysis (FMEAs) or some equivalent.

The FMEA process or similar evaluation requires hundreds to thousands of hours of intensive investigation by specialists from the developer supplier and device manufacturer. Testing is designed to account for the nature of the change, the anticipated impact on other processes on the production line, the products produced, and other considerations. A typical test program may involve hundreds of wafers (raw material cost $250-500 per wafer) processed side by side with controls and alternatives. At each step along the way, samples are analyzed and often each individual completed package must be electrically tested at the end of the production process.

Requalifications are customer-specific, product-specific, change-specific and, to some extent, production-line-specific. One change, therefore, has implications at all customer sites and production lines, and the costs and efforts associated with that one change can rapidly escalate if the products are used by several customers.

Less complicated developer requalifications require 2 to 4 months of effort. A complex requalification can take 18 to 24 months. It is not uncommon for requalifications to cost several hundred thousand to millions of dollars per customer.

While a rigorous process of this nature was required to qualify a non-PFAS replacement for PFOS-containing developer, this process has yielded an important result since 100% of the developer waste is discharged to water.

7115234