Research Needs Document: ESH

Semiconductor Research Corp. (SRC)
Research Triangle Park, NC 27703

Introduction

Semiconductor fabrication processes have evolved enormously with time, largely driven by the demand for advanced device architectures and increased performance. To continue to drive innovation and to achieve the desired electrical functionality required by today's market, the industry relies on a number of highly sophisticated chemicals and materials. However, the potential environmental, health and safety issues associated with the use of some new chemistries may not be fully available or understood at the time our suppliers introduce chemicals to the market. This requires the industry to invest in proactive environmental, safety, and health (ESH) research and development (R&D). Proactive ESH R&D is necessary to enable new technology, address new information from evolving health and environmental science studies, assure compliance with government regulations, and prevent the need for expensive and disruptive corrective measures.

This *research-needs* document identifies materials of high concern (MoHC) that we believe need to be evaluated and addressed proactively with ESH R&D. Where feasible, safer more benign substitutes should be developed for MoHC. Where substitution of a more benign material is not feasible, process technology should be developed and optimized for minimal use with maximum protections that mitigate risks. Likewise, cost-effective treatment and abatement processes are needed to assure that wastewater effluents, air emissions, and other waste streams, all have minimal environmental impacts.

The ESH R&D needs are addressed in four sub-categories as follows:

5a) ESH impact analysis of materials.
5b) Aqueous effluent management.
5c) Air emissions management.
5d) Alternative materials analysis.

5a) ESH impact analysis of materials.
New and novel chemicals are introduced to the semiconductor industry by chemical and tool suppliers at a rapid rate that sometimes outpaces the rate at which the suppliers can provide fundamental information on the physicochemical properties, toxicity, and environmental fate and behavior characteristics of the purchased chemicals, and/or the reactive products that are created within manufacturing processes. This can lead to unanticipated hazardous conditions, and/or unexpected regulatory actions on chemicals used in critical applications. In light of these concerns, proposals are encouraged that provide knowledge and solutions for the following:

- **Evaluate EUV and other photoresist chemistries for toxicity, environmental fate and behavior characteristics**. A wide variety of potential resist chemistry systems are under evaluation for EUV and other photolithography applications. These include conventional triarylsulfonium and diaryl iodonium type resists, as well as novel metal-based nanoparticle resists, among others. A systematic evaluation of potential emissions, occupational exposure routes, and waste streams of the resist compounds, degradation by-products produced as a result of the manufacturing process and by-products created during biotic and abiotic processes could help fabs and photolithography suppliers assure that effective controls are available and in place to enable the continued safe use of these rapidly evolving technologies. In addition, a better understanding of the effect of structural modifications (i.e., the cation, alkyl chain length, functional groups, anion) on the overall toxicity potential and environmental fate and transport of onium photo acid generators and all stable chemical species generated from the manufacturing process to the mineralized elements would be useful for identifying structural classes that may have the potential to pose a greater risk to human health and the environment.

- **Development of predictive toxicology tools for cationic species.** Currently, there is a lack of appropriate *in silico* models available to delineate the toxicity potential of some cationic species such as those commonly used in certain photolithography applications (e.g., triarylsulfonium and diaryl iodonium). Developing computational methods for estimating the toxicity potential of these chemicals would be useful in identifying safer more benign substitutes, where feasible.

- **Develop information regarding the behavior, toxicity, treatment, and monitoring of per- and polyfluorinated chemicals used in photolithography.** The semiconductor industry and its suppliers have worked hard to minimize and/or eliminate the use of long chain perfluorochemicals like PFOS and PFOA because of their defined environmental and health risks. However, in the meantime, thousands of new PFAS compounds have been introduced to commerce, many under the claim of being safer and more environmentally benign, but few with definitive data to back the claims. For instance, recent information and controversy over short chain fluorinated chemicals like Gen-X highlight the need for chemical substitutions to be well informed and backed by solid data. Research that provides fundamental data on the behavior, toxicity and fate of per and polyfluorinated chemicals that are in current use and/or targeted for future use in photolithography would be very valuable. In addition, understanding what attributes are most important for determining the toxicity potential of these compounds would be helpful in identifying more benign substitutes, where feasible. This could include both literature search and analysis of existing information as well as the testing of less common, or minimally tested PFAS used in the semiconductor industry. It will also be helpful to validate (e.g. NIOSH) exposure monitoring methods for the per- and polyfluorinated chemicals currently used in photolithography. Proposals should clearly articulate how the proposed work would produce actionable information that the industry can put to effective use. PIs are encouraged to partner with photolithography suppliers, device makers, and/or government institutions to who are all simultaneously trying to better understand this class of chemicals.

- **Evaluate availability and capability of analytical methods that address the industries need to measure and control chemicals of concern in our working environment, wastewater and air emissions streams, that would provide rapid, if not real time, measurement capability for PFAS-as-a-class, TMAH, nMP, azoles, HF, nanoparticles, total oxidizers (H2O2 + H2SO4) and other constituents of concern.** At present our efforts to measure and control these types of materials in our waste and emission streams is thwarted by the availability of analytical methods, and laboratories that can support our evolving needs with timely, high quality measurements. Effort should focus on common semiconductor chemicals (e.g. PFASs, TMAH, nMP, HF, etc.) and categorically focus on total organic fluorine, organics, fluorides, caustics, nanomaterials, etc., to test for varying chemicals in any exposure scenario, or for monitoring of emissions and effluents. Efforts should include the evaluation of capability to do both in-lab analytical analysis of samples, as well as evaluation of small-scale detectors for integration into light weight, highly portable detection devices, or for use as standalone devices, which can provide detection of multiple types of chemicals simultaneously, or have the flexibility to interchange detectors suited to the material being tested. Such detectors may require an evaluation method that includes secondary testing beyond the manufacturer for target chemicals. Developed detection methods should be validated methods (e.g. NIOSH).

5b) Aqueous effluent management.

A number of common wastewater constituents represent emerging concerns because of their bioinhibitory, refractory, and/or potential PBT characteristics. Potential chemicals of concern include PFAS, PAG cations, azoles, and TMAH, among others. Often the chemicals of concern may occur at very low concentrations in waste streams that have very high flow rates, such that destructive treatment of the targeted chemical may not be viable without the use of a process step that removes and concentrates the chemical of concern for cost effective destructive treatment. Also, it is our general experience that the viability of a wastewater treatment process is often highly dependent on the presence and composition of other constituents that occur in a wastewater, in addition to the designated target compound. It is essential therefore that wastewater technology development addresses real fab wastewater early in the game. In light of these considerations, proposals are encouraged that:

- **Develop technology and information for effective wastewater treatment of residual photolithography effluent streams.** The vast majority of photoresist and PAG is recovered into solvent waste systems for recovery or incineration, with only a small quantity of residual organics reaching wastewater streams through the developer step, and post resist strip rinses. Additionally, in a small number of scenarios an aqueous photoresist system exists where all waste goes to the industrial wastewater. Despite the low expected concentrations, a consortium of semiconductor manufacturers and photolithography chemical suppliers are currently working with the US EPA and a university to investigate new concerns regarding the toxicity and environmental fate and behavior of onium based photoacid generator compounds (PAGs). Depending on the results of these investigations, there may be a need to develop cost effective technology for the removal of these compounds and/or their photodegradation products from complex fab wastewater streams. Investigation into removal of very low concentrations of organic cations such as triphenylsulfonium, or a substituted diphenyliodonium or triphenylsulfonium from a wastewater drain system that contains very high concentrations of tetramethylammonium cation will be necessary.

- **Develop and/or validate effective and complete destruction of organic per- and polyfluorinated chemicals and gases (PFASs & PFCs) in incineration and fuel blending operations.** At present there is equivocal information regarding the temperature, residence time and potential other process conditions necessary to assure effective and complete destruction of perfluoroalkyl substances (PFAS) and PFC gases in a manner that does not generate significant amounts of undesirable daughter products such as CF4 and C2F6. Ideally, the project would include commercial scale test runs as well as laboratory and theoretical evaluations. Also, to ensure that other criteria pollutants are minimized, e.g. NOx, SOx, CO, PM (particulates), and Volatile Organics.

- **Develop information that fabs and POTWs can use to determine what organic chemicals can be effectively treated by biotreatment processes.** Currently there is uncertainty and/or equivocal information regarding the extent to which residual organic chemicals like nMP, TMAH, azoles, and isothiazolinones, amongst others; can be effectively treated in the conventional activated sludge processes used by most POTWs that receive residual fab wastewater. It is generally appreciated that the ability of a particular POTW to treat an organic chemical may vary with SRT, biomass, target chemical concentration, and other factors; but these factors--and how they vary between chemicals and as a function of POTW design and operating conditions--are poorly characterized. PIs are encouraged to partner with device makers and/or government POTWs to better characterize and test capabilities of sludge in treating such chemicals.

- **Evaluate/develop concentrating techniques for separation of water and solvents.** Separation of mixtures that are of near equal proportions of dissimilar chemicals, e.g. 50:50 water/organic, 50:50 of organic/inorganic, and proportional levels of sulfuric acid and peroxide can be difficult to treat. Ultimately the difficulty in treating these chemicals leads to increased costs, inefficient waste treatment, and increased hazardous waste generation. Some mixtures, like those containing high peroxide concentrations can be unstable and represent reactive safety hazards. Understanding possible solutions, including both static and dynamic (in-line) separation techniques for these common scenarios would be helpful to better control the resulting necessary treatment scenarios, and reduce hazardous waste.

- **Evaluate the driver for increasing use of organic cleaning solvents.** The industry has shifted over time from aqueous and inorganic cleaning agents to organic and organic/inorganic mixtures for newer technologies. It would be helpful to understand technology drivers for increased uses of organic or organic/inorganic mixes of cleaning chemistries, including the physics and surface science behind this change. PIs should also investigate technically viable alternatives and optimization techniques that could reduce the use of these types of substances, and/or shift to alternatives that are "greener" and have a lower total cost of ownership.

5c) Air emissions management.
Cost effective treatment of fab air emissions have become an increasing challenge. One challenge is the recent focus on the use of absolute rather than normalized Global Warming Gas (GWG) reduction targets. Other challenges include the limitations in emissions measurement capabilities, and an absence of demonstrated cost effective abatement solutions for

some common chemicals that are used and/or generated in semiconductor device manufacturing. In light of these considerations, proposals are encouraged that:

- **Investigate better air emission measurement techniques than FTIR on stacks (for example on Cl2 or PFAS).** Dilute emissions are difficult to quantify using FTIR or other EPA-preferred analytical techniques. Specialty materials are driving the need for a better measurement technique. Currently equipment clogging and sampling size limitation are the primary issues with FTIR that need remedy. Improved online (real-time) capability is needed.

- **Evaluate methods for N2O removal from air emissions.** N2O is one of the largest unabated GWG emissions in the industry. There is a need for effective N2O reduction systems that do not produce large amounts of NOx. It would be helpful to understand information on potential catalytic and other transformation capabilities that might lead to more efficient use with lower operating costs. PIs should consider engaging/partnering with abatement system vendors to comprehend current capabilities and gaps of leading-edge equipment. PIs might also want to consider this topic in combination with the next topic, NOx abatenment.

- **Investigate NOx Abatement options for end of pipe treatment or POU.** Many end-of-pipe or point-of-use treatment devices use burn abatement to treat target emitted chemicals. The increasing use of these types of treatment devices is leading to a significant production of NOx. It would be helpful to develop information on generation and/or behavior in typical semiconductor abatement systems and evaluate various mechanisms to eliminate generation of NOx or derive options to convert NOx to a non-regulated species.

- **Evaluate Low to zero GWP heat transfer fluids (HTFs) for Semiconductor equipment chiller use.** The goal is to find a material(s) with Low GWP that also meets a wide range of performance requirements as do current higher GWP chemicals, which aren't also other criteria pollutants (e.g. volatile organic compounds [VOCs]). The upper performance range of existing Low GWP materials are typically 30-50 degrees lower than current Higher GWP materials. HTFs represent a very large portion of the GWGs pareto – EPA estimates 13-15% of U.S. total, so the opportunity is quite large to find better HTFs. PIs might consider working with Tool/Equipment suppliers such as Applied Materials, LAM Research, Tokyo Electron (TEL), etc., as well as device makers to evaluate options.

- **Evaluate cleaning-time changes to yield in plasma tools - characterize how to set end of recipe limits.** Nozzle flushing (at start) and post endpoint for cleaning/etching uses tend to use excessive quantities of PFCs leading to higher emissions. Excessive run-time on such recipe steps is typically related to fear of yield issues. PIs will develop appropriate empirical models for predicting optimal use of PFCs for non-processing/cleaning steps on CVD/Etch tools.

- **Evaluate methods and technologies for exhaust switching.** Semiconductor tools have multiple chemistries, and therefore multiple exhaust system connections that require exhaust switching to go to appropriate relative treatment systems (i.e. for deposition tools). The focus should be on evaluating reduction or elimination of dragout of chemicals to inappropriate exhaust connections which can have negative effects such as reduction in 'house' abatement removal efficiency and fouling. PIs should consider engaging/partnering with exhaust/abatement system vendors to comprehend current capabilities and gaps of leading-edge equipment.

- **Develop and/or validate effective and complete destruction of organic per- and polyfluorinated chemicals and gases (PFASs & PFCs) in incineration and fuel blending operations.** [Please see combined needs in aqueous effluent management section above.]

5d) Alternative materials analysis.

The industry strives to use the most benign material that is effective for a given application. However, the task of identifying, demonstrating, and implementing more benign and cost-effective substitutes is challenging. Projects that develop fundamental information on chemical behavior, process technology, and/or toxicity help pave the pathway for innovation. The ideal projects might involve partnering with a chemical or tool supplier who can help demonstrate the technical viability of proposed alternatives. We encourage research proposals that:

- **Evaluate alternative etchant or cleaning gases and processes that are effective and safe.** At present, a variety of fluorinated gases like **CF_4, C_2F_6, and SF_6** are used for plasma etching and chamber cleaning. These chemicals can be hazardous, have high global warming potentials (GWPs), and can be difficult to destroy via conventional thermal abatement technology. The evaluation of more fundamentally simple, and high yielding starting gases such as F2 show promise for reducing the amount of PFC emissions. These technologies are somewhat new, and need evaluation of their performance capabilities, safety considerations, emissions factors, and operational sustainability in order for the industry to adopt their use more broadly.

- **Evaluate alternatives for more benign photolithography formulations**: Reduction or ideally elimination of PFAS from photolithography formulations could help the industry reduce its environmental footprint and costs, if more benign, and equally effective substitutes can be identified and implemented. The ideal project would involve partnering with a photolithography chemical supplier and/or fab who can help demonstrate the viability of proposed alternatives at the wafer-level on tools.

- **Evaluate more benign and/or easily treatable metal passivating agents.** Currently a wide variety of azoles compounds are used in CMP and wet chemical processes to aid in selective etching/materials removal. However, azoles are potent nitrification inhibitors, biorefractory, and may exert aquatic toxicity. The development of more benign metal passivating agents could save millions of dollars per year in waste treatment costs. Likewise, the development of fundamental information regarding the mechanism by which metal passivating agents work in CMP, wet chemical, and corrosion control might lead to more effective, efficient and benign applications.

- **Investigate availability of more benign or easily treatable biocides.** Currently a variety of biocides, including various isothiazolinones, are used to prevent microbial growth in carbon-rich wet chemical formulations, and to protect cooling water and cooling tower systems. However, these can be potent nitrification inhibitors, biorefractory, and exert aquatic toxicity. Fundamental information on the use, mode of action, and behavior of biocides may aid in developing more efficient dosing and blowdown regimens. Likewise, the development of more benign and/or readily treatable biocides could save millions of dollars per year in waste treatment costs.

- **Evaluate less-toxic substitutes for TMAH (tetramethylammonium hydroxide).** TMAH is a strong organic base that is in widespread use as developer and in various wet etch applications as both etchant and pH adjuster. In general, there is a need for strong organic bases that can be used in applications like silicon etching and other wet chemical formulations and photolithography. Fundamental studies on the mechanism of TMAH toxicity may also be of interest to the extent that they help the industry identify more benign alternatives and/or improve the protections and controls on existing uses of TMAH.

- **Evaluate alternatives to nMP for use in photolithography.** Currently nMP is the subject of an EPA risk analysis, and there is a desire for more benign alternative solvents that still achieve effective cleaning of photomasks and other organic thin films. An evaluation of various proposed alternative chemistries needs to be conducted for common semiconductor applications to establish technical feasibility and reliability.

- **Evaluate alternatives to N2O for use in deposition.** N2O is one of the largest unabated GWG emissions in the industry. An evaluation of other feasible deposition mechanisms for leading edge semiconductor use that reduces or eliminates N2O needs to be conducted to establish technical feasibility and reliability.

Contributors

Reed Content (GLOBALFOUNDRIES)
John Currier (Intel)
Chris Lee (TI)
Bob Leet (Intel)
Jennifer Politsch (Intel)
Farhang Shadman (U Arizona)
Dave Speed (GLOBALFOUNDRIES)
Brooke Tvermoes (IBM)
Sarah Wallace (TI)
Kevin Wolfe (Intel)
Tim Yeakley (TI)